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PRELIMINARY RESULTS ON THE COLOR OF NEBULAE

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Important differences in the spectra of gaseous nebulae, even those of the same general class, have been known for many years. Although the characteristic nebular lines λ 5007 and λ 4959 seem to maintain a constant ratio of brightness, their behavior varies greatly with respect to $H\beta$, λ 4686, λ 3727, and other lines. Thus $H\beta$ is usually fainter than the chief nebular line λ 5007, but there is a wide range in the relative intensities, and intensity reversals may even occur. Again, lines usually present are as yet unobserved in certain objects, and in some we have apparently only the monochromatic radiation λ 3727.[1]

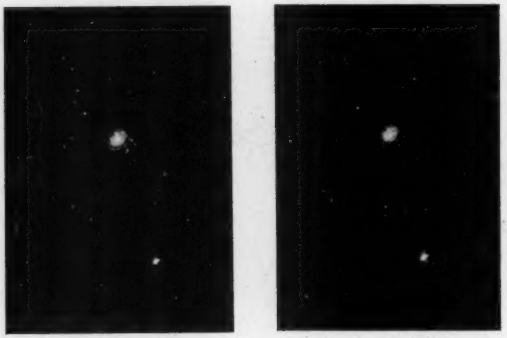
This diversity is reminiscent of the differences in the spectra of stars. These are universally accepted as evidence of evolutionary change, and if nebulae have any part in the scheme of development, it is likely that their spectral peculiarities will find a similar interpretation. In this event spectral correlations must exist, more or less clearly defined according to the development of the nebulae compared. The important investigations of Wright have already revealed relationships presumably of this kind.

Further, experience in other fields suggests the probability of spectrum differences within the same nebula. No mixture of luminous vapors is homogeneous in its radiation, for the pressure, temperature, electrical conditions, etc., are never constant throughout. Thus the spectrum changes from point to point in the flame and the electric arc; the radiation from the attenuated gases of a vacuum tube varies with the region examined; and, on a larger scale, the spectrum of the corona, the chromosphere, and the reversing layer—or, even better, spectroheliograms

for hydrogen and calcium—reveal the selective distribution of vapors within the solar atmosphere.

Lack of homogeneity has already been observed in numerous nebulae; but probably the phenomenon is more nearly universal than has hitherto been supposed, and one naturally inquires whether internal differences may not provide useful criteria of development supplementing those based on spectral variations from nebula to nebula. In fact Wright has already called attention, in the case of planetary nebulae, to the gradually increasing concentration of λ 4686 within the nucleus as we approach the Wolf-Rayet stars in his graded series of spectra.[2] He has made this circumstance a basis for classification, and it seems likely that such criteria will be even more used in the future.

Various methods for investigating the constitution of nebulae are available. Measures with a spectral photometer should reveal differ-



Seed 27 10^m Iso 1^h

FIG. 1. MESSIER 51.

ences in the distribution of the gases; but few objects are bright enough for an application of the method, which at best is tedious and uncertain. Monochromatic photographs for each spectrum line can be obtained with a slitless spectrograph or an objective prism; but if the nebula is large, or the dispersion insufficient, the images overlap. The method is useful for planetary nebulae, which are small and relatively bright. For these the ordinary slit spectrograph gives valuable results, the distribution of luminosity being indicated by the length of the lines. That localized in the nucleus produces short lines, while longer lines originate in gases more widely distributed. The method has been used effectively by Campbell, Wright, and Wolf.

For a general survey photographs on ordinary and photovisual[3] plates should yield useful information. This method was first used by

Keeler[4] to confirm Campbell's results for the nebula in Orion. It shows admirably, but without differentiation, the distribution of whatever luminosity lies between the limiting wave-lengths determined by the filter and the color curve of the plate. Some refinement of analysis can be effected by using filters of limited transmissibility. Thus Hart-

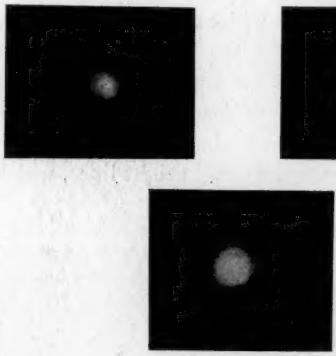


FIG. 2. MESSIER 94.

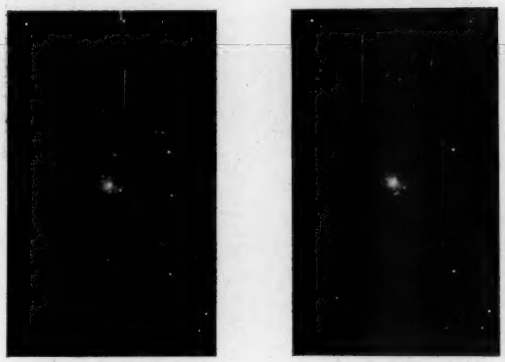


FIG. 3. MESSIER 99.

mann[5] showed that the great photographic activity noted by Keeler in certain regions of the Orion nebula is due to λ 3727, whereas the wider spectral region embraced in Keeler's photographs left the identity of the active radiation in doubt. Again, a red-sensitive plate and a filter transmitting nothing to the violet of λ 5600 enabled Hale[6] to demonstrate the reality of the reddish fringe observed by Barnard, and later by

Keeler, along the southern boundary of the Huyghenian Region, and to show that the color was probably due to the $H\alpha$ line of hydrogen. Spectrum photographs by Adams subsequently placed the matter beyond doubt.[6]

The usefulness of monochromatic photographs seems thus to have been demonstrated, but it does not appear that they have been employed except for the Orion Nebula. A wider application has therefore seemed desirable, particularly for objects too faint for detailed spectroscopic observation. Among these one naturally turns to the spiral nebulae because of the unexpected result uniformly found for the central region, namely, an absorption spectrum of intermediate or late type. Even admitting the presence of superimposed bright lines, which has in some

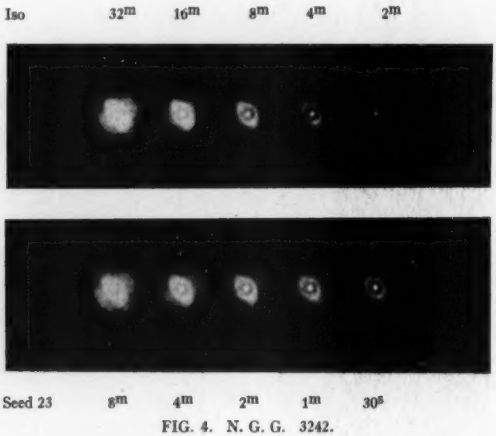


FIG. 4. N. G. G. 3242.

cases been claimed, the result is still remarkable for objects whose finer details are suggestive of some of the gaseous nebulae.

The illustrations show the distribution of the blue and yellow light in three of the well-known spirals, Messier 51, 94, and 99. The photographs were made with the 60-inch reflector on Seed's '27' and Cramer's 'Instantaneous Isochromatic' plates, the latter exposed behind a yellow filter. The exposure time for yellow light was six times that for blue, in order that the images for the bluer stars might be comparable on the two photographs.

Few if any of the yellow images are smaller than the corresponding blue images, at least for objects which are certainly stars; but this is by no means the case for the condensations and nebulosity comprising the branches of the spirals. For these the relative weakness of the

yellow light is a striking feature for each of the objects mentioned. Quantitative measures of intensity have not yet been made, but there is every reason to believe that the nebular condensations will reveal negative color indices of large amount. The knots of nebulosity are certainly bluer than the bluest of the neighboring stars, and one is reminded of the great photographic activity of the central star in the Ring Nebula in Lyra.

Whatever the spectral character of these outlying regions may prove eventually to be, it must differ from that of the central nucleus, for the three central nuclei and the secondary nucleus at the end of one of the branches of M 51 are all much stronger in yellow light than in blue. Here the color seems to be in accordance with the typical absorption spectrum found in all similar objects thus far observed.

It is still too early for any general conclusion, but preliminary photographs of other spirals suggest similar results; and it seems not unlikely that the phenomena described are typical of this class of objects.

In contrast to the spirals it is of interest to note the results for the bright planetary N.G.C. 3242, which is also illustrated. In this instance no important differences are revealed by the blue and yellow exposures, at least none which cannot be accounted for by possible differences in gradation on the two kinds of plates.

[1] Newcomb-Engelmann, *Populäre Astronomie*, Fünfte Auflage, p. 672, Leipzig, 1914.
[2] These PROCEEDINGS, **1**, 590 (1915).
[3] An isochromatic plate exposed behind a yellow filter.
[4] *Astroph. J.*, **9**, 133 (1899).
[5] *Ibid.*, **21**, 389 (1905).
[6] An unpublished result obtained in 1909.

THE ACTION OF ALKALI IN THE PRODUCTION OF LIPOLYTICALLY ACTIVE PROTEIN

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Introduction.—A summary of an extended experimental study of the lipolytic or ester-hydrolyzing enzymes was presented in these PROCEEDINGS last year.[1] The changes in the lipases themselves under various conditions were the main objects of the investigation at that time, as a preliminary to the possible elucidation of the chemical structure of the active groupings. The investigation of the factors which control the loss or destruction of this enzymatic hydrolyzing activity

appeared to offer the most promising field for further study; a preliminary report on the results of this study is here presented.

The materials used were *Esterase preparation*, a clear, dialyzed and filtered water-extract of oil-free and husk-free castor beans 0.5 g. to 60 cc.; and *lipase preparation*, a mixture from the 1.5 normal NaCl solution extract of water-extracted castor beans, 1.0 g. to 100 cc., dialyzed until salt-free. The former, a clear colorless solution, was more suitable for following the changes under different conditions than the latter, which was a suspension of globulin in water.

The activity tests were carried out with 1 cc. ethyl butyrate or 0.5 cc. glyceryl triacetate at 38° for 24 or 48 hours, and the results given as the number of cubic centimeters of 0.1 normal alkali required for neutralyzing the acid produced with phenolphthalein as indicator, with suitable corrections for blanks.

Inactivation of the enzymes by acid.—The hydrogen-ion concentrations were determined by color comparison with the standard solutions and indicators recommended by A. A. Noyes.[2] The esterase preparation, $H^+ = 10^{-7.0}$, brought to $H^+ = 10^{-3.5}$ with acetic acid for 24 hours and then back to $H^+ = 10^{-7.0}$, lost its activity completely. At $H^+ = 10^{-4.5}$ under the same conditions for the same length of time, one-third of the activity was lost, while at $H^+ = 10^{-6.0}$ about one-eighth was lost. The difficulty of color comparison with the lipase preparation made difficult an exact determination of the H^+ ion concentration at which inactivation took place. A larger H^+ ion concentration than with the esterase preparation appeared to be necessary to produce a corresponding effect.

Inactivation by alkali.—The esterase preparation lost one-eighth of its activity after being kept at $H^+ = 10^{-8.0}$ for 24 hours, and became practically inactive at $H^+ = 10^{-10.5}$ and $10^{-11.0}$. The lipase preparation dissolved to form a cloudy solution at $H^+ = 10^{-11.0}$. Kept at this for 18 hours and then brought back to $H^+ = 10^{-7.0}$, one-half of the activity was lost. At about $H^+ = 10^{-12}$, one-third of the activity remained, and at about $H^+ = 2 \times 10^{-12}$, one-sixth remained.

Inactivation by alcohols and by acetone.—It was shown previously that dilute solutions of methyl alcohol, ethyl alcohol, and acetone inhibited the action of both preparations. Solid preparations made by precipitation and washing with alcohol were always inactive. Solid esterase preparations, precipitated and washed with acetone, were active in a number of cases; but the activity was much smaller than that of the corresponding solutions from which they were prepared. Similar solid lipase preparations were always inactive.

Inactivation by salts.—The action of salts on these enzymes has already been described. Some produced marked inactivation, others less, while some accelerated the hydrolytic actions.

Inactivation by heat.—Like all enzymes, the esterase and lipase are both inactivated by heating their aqueous solutions or suspensions for a few minutes at 100°. The original oil-free and husk-free castor beans, on being heated dry at 100–110° lost 50–80% of their lipolytic activity; the same loss of weight in a vacuum desiccator over phosphorus pentoxide was not accompanied by loss in activity. Drying first, and then heating (the latter causing only 0.1–0.2% greater loss in weight) produced 50–80% loss in activity.

Nature of the chemical changes involved in the inactivations.—The summary of the different ways in which the esterase and lipase preparations may be inactivated makes it appear at first sight as if different reactions occurred in the inactivations. If, however, a definite chemical group is responsible for a definite enzyme action, it might perhaps be more reasonable to assume that inactivation followed a definite reaction. The preparations were essentially protein in character. There is no evidence that a dehydration, or loss of the elements of water, causes the inactivation. Some of the reactions indicate that a possible hydrolysis may be a cause of inactivation. With proteins, hydrolysis is generally taken to occur with the – CO–NH – group, which goes over into the – COOH NH_2 – groups. Experiments with all the inactivations showed in no case an increase in the formal titration as would be expected in such a reaction, and therefore makes the assumption of such a hydrolysis improbable. Coagulation of the material accompanied some of the inactivations. This physical change alone does not appear satisfactory as an explanation, some change in chemical structure unquestionably accompanying or producing the physical phenomenon. Furthermore, the lipase material in suspension in water showed the same activity as in 1.5 normal sodium chloride solution when tested immediately.

The explanations of the chemical changes accompanying inactivation so far suggested are not satisfactory. The reagents used are simple. It is difficult to conceive of a very deep-seated chemical reaction taking place under so many different conditions, none of a complex nature. To the writer the only chemical change which appears probable under these conditions is that involving a simple rearrangement within the molecule, such as a tautomeric change involving the change in position of a hydrogen atom. In considering the structure

of proteins, it is evident that such a rearrangement is possible in the peptide linking.

The hypothesis to be suggested is that the active grouping of the esterase and lipase preparations is of the enol structure $-C(OH)=N-$, the specific actions being dependent in part upon the groups combined with the C and N, and that inactivation consists primarily in a rearrangement to the keto group $-CO-NH-$. Such structures have been proposed at different times as indicating the difference between proteins in living matter, and proteins not in living matter.

Since strong alkali, as a rule, favors the formation of the enol structure in such tautomeric changes, a way is open to test the hypothesis.

Activation of proteins by alkali.—One gram of inactive solid lipase-preparation, washed and dried by means of alcohol, was allowed to stand 24 hours with 25 cc. 10% NaOH solution (and toluene). The brown suspension or mixture was diluted with 100 cc. water and dialyzed against running water for 24 hours to remove the greater part of the alkali. The volume increased to 410 cc. The mixture was brought to a very faint pink color toward phenolphthalein with hydrochloric acid, and the hydrolytic action of 50 cc. portions (corresponding to 0.12 g. original material) was tested for 48 hours. An action (corrected for blanks) of 0.24 cc. was found with ethyl butyrate, and 0.73 cc. with glyceryl triacetate.

Many experiments were also carried out with casein (Kahlbaum's preparation "nach Hammarsten"), of which the following may be cited. Two grams of casein were mixed with 25 cc. 1 normal NaOH solution (and toluene). After 24 hours at room temperature, a grayish-brown and dialyzed 48 hours, the volume increasing to 280 cc.; the H^+ ion concentration was then brought to $10^{-7.0}$, and the hydrolytic actions of 40 cc. portions, corresponding to 0.3 g. of casein each, were tested for 48 hours. The actions found were 0.08 cc. with ethyl butyrate and 0.48 cc. with glyceryl triacetate. A large number of similar experiments were carried out in which the alkali was removed either by dialysis alone or by direct neutralization with acid. There was marked action on glyceryl triacetate, but only very slight action on ethyl butyrate.

The strength of the alkali, between 0.1 normal and 3 normal, used in the preliminary treatment, appeared to have small influence on the activity produced; but great influence was exerted by the H^+ion concentration of the solutions in the activity tests. This last effect may be shown by a series of results with 1 normal NaOH solution in which

the alkali was neutralized directly to different points. Twenty-four hours' action on glyceryl triacetate gave the following results:

H^+ ion concentrations	10^{-4}	10^{-6}	10^{-8}	10^{-10}
Activities	0.15	0.10	1.17	1.47

Two similar experiments gave the following results:

H^+ ion concentrations	10^{-7}	10^{-8}
Activities	0.91	1.68

The action was therefore greater in slightly alkaline solution.

[1] These PROCEEDINGS, **1**, 136 (1915).
[2] *J. Amer. Chem. Soc.* (1911).

THE EXCRETION OF ACIDS BY ROOTS

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Whether roots excrete acid, other than carbonic, has long been a matter of controversy. The problem is important not only because acids dissolve plant food from the soil, but also because it involves the fundamental questions of the reaction of protoplasm and of the mechanism of secretion.

The problem has been greatly complicated by the failure of many investigators to distinguish between the effects of dead and of living cells.

Becquerel early pointed out that all seedling roots when laid on moist neutral litmus paper possess the property of giving it a lasting red color, which he believed was due to excretion of acetic acid. Boussingault thought that the acid might be lactic, while other investigators left the nature of the acid undetermined. The alkali salts of formic acid have been reported by Czapek[1] in the culture solution of *Lepidium* and *Hordeum* seedlings. The formic acid was considered as coming not from the root hairs but from the sloughing off of root cap cells and their secondary decomposition. The drops occurring on root hairs in a moist atmosphere were found to give no acid reaction. The solvent[2] action of plant roots has been considered to be due not alone to the respired CO_2 but also to organic acids because phosphorite (which can be taken up to some degree by plant roots), requires a strong acid to dissolve it. Kunze[3] believes that there is no free mineral acid in the root excretion of higher plants, but that the acid reaction is due to

organic acids and that the quantity of detectable acids is very small, lying below the limit of sensitivity of litmus. Czapek[4] concluded that roots gave off K, Ca, Mg, HCl, H_2SO_4 and H_3PO_4 to water. Stocklasa and Ernest[5] have been unable to find K or H_3PO_4 in root excretions. They found that CO_2 is the only gaseous product in root excretions, with a possibility of H. No free mineral acids were considered to be present in root excretions, and organic acid excretion was considered to occur only when the oxygen percentage was low. Breazeale and LeClerc[6] state that the roots of wheat seedlings in distilled water excrete acids other than CO_2.

In some of the investigations mentioned above no control of distilled water without seedlings was run, and the amount of alkali used to titrate a boiled sample of distilled water, in which seedlings had grown, appears to be approximately the amount required to cause coloration of the indicator in such a volume of neutral solution. Seeds were in some cases in contact with the solution and might have given off acid from dead cells. In some cases it appears certain that dead cells of the roots affected the results. The use of carbon black by some investigators introduces an unknown factor which may alter the results.

The experiments of the writer were made upon early sweet corn by soaking the seed for several hours and then germinating it on moist filter paper in porcelain pans covered by inverted pans. When the roots were about one to one and one-half inches long, the seedlings were placed in the water cultures. Glass tumblers were steamed and thoroughly cleansed, and the outside covered with paper to prevent the growth of algae. Dental napkins, in which one rather large and numerous small holes were cut, were used to cover the tumblers after the distilled water was run in.[7] The cloth covers were drawn tight by the use of string and never were allowed to come into contact with the solution. The larger hole was used to run in more water as evaporation proceeded while in the small holes the seedling roots were placed. Covers of various kinds were used because the water evaporated too rapidly from the tumbler through the cloth. The same kind of cover, with a thin coat of high grade paraffine, prevented much evaporation since the large corn seed covered the hole through which the root had been thrust. Also no tying of the cover was necessary; simply folding down the overhanging edges of the cover about the sides of the tumbler sufficed. Great care was taken to use only roots which had no dead cells (except those of the root cap).

Experiment 1. Twenty-five seedlings were grown in each tumbler in 190 cc. of distilled water. Controls were set up similar in every re-

spect (except that they contained no seedlings) and having the holes in the covers partially covered so as to obtain about equal amounts of evaporation in all the tumblers. A series of phosphate buffer solutions, of known hydrogen ion concentration, and checked by the use of the gas chain, were made up. Phenolsulphonephthalein (12 mgm. per 100 cc.) was used as indicator (3 drops to 10 cc. of solution). The indicator was added to a series of tubes containing the various buffer solutions whose PH^+ value was known.[8] After the plants had grown for 8 days, 10 cc. of the water from each tumbler was run into a tube of the same diameter as those containing the buffer solutions and after adding 3 drops of the indicator, the CO_2 was expelled by a stream of hydrogen (washed free from impurities). The hydrogen was allowed to run through each tube for one-half to three-quarters of an hour to be sure of expelling all the CO_2.

TABLE 1

Results after CO_2 was expelled

Water from tumblers containing roots	Water from controls without plants
1. P_H+ 7.38	1. P_H+ 7.38
2. " 7.38	2. " 7.38
3. " 7.38	3. " 7.38

Experiment 2. Seedlings with vigorous roots and with apparently no dead cells, were grown for 5 days in culture. The distilled water was different from that in Experiment 1.

TABLE 2

Results after CO_2 was expelled

Water from tumblers containing roots	Water from controls without plants
The water from 7 tumblers each P_H+ 7.16	The water from 6 controls each P_H+ 7.16

A similar experiment in glass tumblers was run for 19 days. During that time the cultures received no attention whatsoever. Analysis showed no increase of acidity, even though the roots were full of brown spots.

The use of glass tumblers might be objectionable because of the possible dissolving of the glass, resulting in the possible neutralization of any excreted acid, but in that event the controls ought to indicate an increased alkalinity.

The experiment was then repeated, using large quartz dishes instead of glass tumblers. The covers were made of large sheets of filter paper impregnated and coated on both sides with a thin layer of high grade paraffine, melting point 60–62°C. Holes of the required size were cut out of the cover with a sharp cork borer. The cover was laid on the

dish after the distilled water had been added, and care was taken not to let the cover touch the water at any time. The two quartz dishes each contained 650 cc., and two smaller quartz dishes each contained 50 cc. of pure distilled water. One of the large quartz dishes had 65 corn seedlings growing in it while the other had 77 seedlings. The seeds never came in contact with the water. The seedlings were grown in the culture for 7 days. The water in the dishes was made up daily to the same volume as at the start and the evaporation was kept approximately the same in each dish by covering or uncovering the extra holes in the covers. At the end of 7 days the corn roots were about 6 inches long and apparently free from brown spots. The water was then tested as in the other experiments, the CO_2 being expelled from the samples by running hydrogen (free from impurities) through them for 45 minutes each.

TABLE 3

Results after CO_2 was expelled

Quartz dishes containing seedlings	Quartz dishes containing only water
65 seedlings: Water P_H+ 8.04	No seedlings: Water P_H+ 7.88
77 seedlings: Water P_H+ 7.88	No seedlings: Water P_H+ 7.88

The two covers bearing the seedlings were then lifted from the top of the quartz dishes and by means of a sharp razor blade (that had been thoroughly cleansed) the roots were cut off a short distance below the seed and were allowed to fall into the dishes in which they had been growing. The tops and the attached seeds were discarded. The paraffin covers were put on the dishes and the holes in the covers were closed by laying several layers of filter paper over them. After two weeks, numerous brown spots appeared on the roots, and many of the roots became soft and gelatinous toward the tip. After 4 weeks from the time that the experiment was first begun, the water in which the roots were decomposing appeared brownish, but possessed no disagreeable odor. Analysis of the water was made as described before.

TABLE 4

Results after CO_2 was expelled

Quartz dishes without roots: control	Quartz dishes containing cut-off roots
Control quartz dish.....Water P_H+ 7.88	Quartz dish with decaying roots.....Water P_H+ 8.04
Control quartz dish.....Water P_H+ 7.88	Quartz dish with decaying roots.....Water P_H+ 8.04
	Two new samples of water were taken to verify the results:
	Quartz dish with decaying roots.....Water P_H+ 8.04
	Quartz dish with decaying roots.....Water P_H+ 8.04

After the experiment was ended, it was found that the mass of roots was so soft as to be easily compressible by the fingers into a small ball. The solutions were tested with litmus paper prior to taking out the roots from the dishes. Experience with litmus paper has brough out the fact that it may require some time before the paper indicates the reaction of a solution which is close to the neutral point. The water, that contained the decaying roots, gave no evidence of being acid to blue litmus paper even when the water contained CO_2.

The corn seedlings had been used because of the convenience in making cultures, and because of the opportunity to choose only healthy seedlings having no brown spots on the roots. Whenever any brown spots appeared on the roots before the time for the first analysis the culture was discarded.

Having found that no acid, other than CO_2 was excreted from the roots of corn, experiments were made upon wheat seedlings. Porcelain pans (with no spots on the inside of the pan) were used. The pans were about twelve inches in diameter at the top and were quite shallow. The same volume of water was run into each pan. Bronze screening was dipped a few moments into nitric acid and then washed a long time in running water. If any acid had remained adhering to the wire, we should expect to find acid in certain of the pans at the end of the experiment. The screening was dried and then dipped into hot high grade paraffine until the screening was coated. The paraffined screens were placed as covers upon the pans of water but were not allowed to come in contact with the water.

Wheat seeds were soaked over a half day in water and were sown in a uniform layer over four of the screens, the other two screened pans of water being used as controls. In two of the four seeded screens, the screens were purposely pushed down until they touched the water and in these two pans the seeds also were partially in contact with the water. Pans were inverted over the seed until they had germinated and their roots had entered the distilled water. The seedlings were then exposed to the light and the control pans were always treated in the same manner.

The cultures were allowed to grow for four weeks without attention of any kind. The plants had grown about 6–8 inches in height in about a week after germination and then ceased to grow. At the end of the experiment the roots in no case were coiled up but grew straight downward. The roots of the seedlings had softened and were well decayed after four weeks. Analysis of the water was made as in the other experiments.

TABLE 5

Results after CO_2 was expelled

Control (screen not touching the distilled water)	Water P_H + 7.6
Control (screen not touching the distilled water)	Water P_H + 7.6
Pan with seedlings (screen or seed not touching the distilled water)	Water P_H + 8.0
Pan with seedlings (screen or seed not touching the distilled water)	Water P_H + 8.0
Pan with seedlings (screen and seed touching the distilled water)	Water P_H + 8.3
Pan with seedlings (screen and seed touching the distilled water)	Water P_H + 8.2

The experiments with corn seedlings indicate that no acid other than CO_2 were excreted by the roots. The data for corn seedlings shows an exceedingly small increase in the alkalinity of the distilled water when the roots were permitted to decompose in the water. The increase in alkalinity of the one culture, of 65 seedlings of corn in quartz at the end of 7 days, probably indicates the presence of some dead cells that were not apparent. Distilled water, into which only the roots of wheat seedlings extended, showed a very slight increase in alkalinity when the roots had decayed, but when the screen, germinated and ungerminated seeds, and roots were in the water, the increase in alkalinity was slightly greater.

[1] Czapek, F., *Biochemie der Pflanzen*, **2**, 872, 1905.

[2] T. Pfeiffer u. E. Blanck, *Landw. Versuchstat, Berlin*, **77**, 217 (1912).

[3] Kunze, G., Jahrb. wiss. Bot., **42**, 357 (1906).

[4] Czapek, F., Zur Lehre von den Wurzelausscheidungen, *Ibid.*, **29**, 321.

[5] Stocklasa, J., and Ernest, A., *Ibid.*, **46**, 73 (1908).

[6] Breazeale, J. F., and LeClerc, J. A., *Bull. U. S. Dept. Agric. Div. Chem.*, No. 149 (1912). See also Meurer, R., *Jahrb. wiss. Bot.*, **46**, 503 (1909), and Johnson, H. V., *Amer. J. Bot.*, **2**, 250 (1915).

[7] The water was distilled from a glass still (which had been used for some months) without the use of cork or rubber. The first and last parts of the distillate were discarded.

[8] This method was adopted because the indicator must be accurately calibrated by buffer solutions in order to obtain results of any value. Phenolsulphonephthalein is very useful for such investigations.

SPECTROGRAPHIC OBSERVATIONS OF RELATIVE MOTIONS IN THE PLANETARY NEBULAE

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In these PROCEEDINGS, **2**, 129 (1916), we described certain rotation phenomena of the planetary nebula N. G. C. 7009 (R. A. = 20 h. 58 m.), as observed by means of the Mills spectrograph attached to the 36-inch refracting telescope. In the past nine months, as opportunity offered, we have extended this line of investigation to others of the

brighter planetary nebulae. We have employed 3-prism dispersion and cameras either 16 or 32 inches in focal length. The linear dispersions at H_β are respectively 20 and 10 angstroms to the millimeter. Up to the present time thirty-three planetary nebulae have been examined for evidences of rotational effects. These effects manifest themselves by Dopper-Fizeau displacements of the spectral lines with reference to the normal directions of these lines as defined by the lines of the comparison spectra of hydrogen and helium impressed upon the same photographic plates. The general results of this work are briefly summarized below. It is convenient to speak at first of the results as relative motions in the nebulae rather than as rotations, the former being the more general term.

1. Of the 33 planetaries observed, 16 give definite evidence of relative motions, and for 5 others we suspect that the nebular lines are slightly inclined in some cases and distorted in others. For 12 of the 33 observed nebulae no indications of relative motion have been found.

2. Attention should be called to the apparent effect of the size of the nebular images upon the results. For the so-called 'stellar' nebulae, or those whose images are essentially round and less than 5 seconds of arc in diameter, the chances of observing line inclinations or distortions are reduced by two causes: first, our experience with nebulae elliptical in outline has been that the relative motions are most pronounced along the major axes of figure, and in the stellar nebulae the positions of the major axes are unknown; and secondly, the spectral lines from the stellar nebulae are very short. Of the stellar objects only one has certainly shown rotational effects. Seven of the 12 objects mentioned in the preceding paragraph as giving no evidence of relative motion belong to the stellar class.

3. Of the nebulae whose diameters are between 5 and 20 seconds of arc, 7 give certain evidence of relative motion, 3 are suspected and 5 seem to give no evidence.

4. All of the 8 nebulae whose diameters exceed 20 seconds of arc give strong evidence of relative motion.

5. With one or two exceptions, the images of the nebulae in which relative motion has been observed are approximately elliptic in form. The greatest observed effects occur in general with the elliptical forms of greatest eccentricity.

6. The 5 nebulae with diameters between 5 and 20 seconds of arc which show no relative motions are sensibly round, which suggest that the axes of rotation may lie very nearly in the line of sight; in which cases the spectrographic test would not be applicable.

7. About half of the nebulae in which relative motion has been detected give spectral lines of forms and degrees of inclinations which are satisfactorily interpreted as due to fairly rapid rotations of the central parts of the nebulae about axes approximately perpendicular to the longer axes of figure, and slower to rotations of the outer parts of the nebulae. These objects belong in general to the class of smaller planetaries whose diameters are of the order of 10 seconds of arc.

8. Five nebulae, most of which are ring nebulae, give lines which suggest the presence of other form or forms of relative internal motion in addition to those interpretable as rotational.

9. The spectra of 3 of the larger ring nebulae, among them the well-known ring nebula in Lyra, while definitely showing internal motions of considerable magnitude, are apparently not interpretable on a simple rotation hypothesis. If rotation effects exist, they appear to be modified or concealed by some other type of motion whose nature we have not yet determined.

10. The central sections of the lines in the spectra of the ring nebula in Lyra and a few other nebulae, corresponding to the central areas of the nebular images, are of bowed form, convex to the red, and are broadened; the central section of the lines in the spectrum of N. G. C. 7662 (R. A. 23 h. 21 m.) is doubled, with one bowed form convex to the red and the other convex to the violet; and the central section of the lines in the spectra of several nebulae are broadened toward the red. These phenomena, if interpreted as Doppler-Fizeau effects, suggest motion of nebular materials toward the nebular nuclei at the centers of the objects, but the high values of the corresponding velocities make the acceptance of such an idea difficult. However, the hypothesis should at least be given careful consideration.

11. The observations indicate that in the nebulae which are more and more condensed as the center is approached we seem to be dealing with simple cases of rotating bodies whose outer strata rotate more slowly both linearly and angularly than the strata nearer the center. In other nebulae, of the ring form with central nuclei, rotation effects seem to be combined with motions of other nature.

12. Measures of the rotational velocity of a nebula enable us to draw some interesting conclusions concerning its probable mass. Assuming that a particle in a nebula at a given angular distance from the center is moving in obedience to the gravitational force of the central mass, then, if the central mass is assumed to be equal to the mass of our Sun, the maximum distances of 9 nebulae whose relative motions seem to be interpretable as rotations lie between 250 light years and 5

light years. These are improbably small distances. If we assume that these nebulae are at distances of 1000 light years, which we have reason to believe is of the order of more probable distance, the minimum values of their masses, in terms of the Sun's mass, lie between 4 and 210.

13. As explained in the former paper, it is difficult to avoid the conclusion that the so-called ring nebulae are in reality not ring forms in space, but ellipsoidal shells. If these forms are rotating about the minor axis of figure, which also seems highly probable, it is difficult to account for their apparent equilibrium under rotational and gravitational forces: it would seem that the nebular materials in the polar regions—the regions of the extremities of the rotation axes—should be depressed toward the central nuclei. Are other forces, possibly including radiation pressure, involved?

14. Inasmuch as the observer will not in general be situated in the planes of the equators of rotation of the nebulae, the observed rotational velocities are smaller than their true values. On this account the actual masses of the observed nebulae should be greater than the minimum values assigned above. The effect of radiation pressures would likewise make the deduced masses too small. The indications are that the nebulae under consideration are capable of developing into systems much more massive than is our solar system.

NEW DETERMINATIONS OF PERMEABILITY

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The purpose of these experiments was to investigate permeability by new and independent methods, in order to test as far as possible the conflicting views now held by different investigators. For a number of reasons the investigation was confined to electrolytes.

1. A new method of determining permeability was devised, which is independent of other methods. This consists in direct measurements of the rate of diffusion of dissolved salts through a diaphragm of tissue from the thallus of *Laminaria Agahrdii* (formerly identified as *L. saccharina*). Discs of tissue (*E*, fig. 1) were placed between two short lengths of glass tube (*A* and *B*), the ground ends of which were covered with a suitable grease (*F*), and applied to the tissue in such a manner as to make the joint water-tight. One of these cells was closed at the end away from the diaphragm by a rubber tube and pinchcock (*C* and *D*). The 'lower cell' thus formed was filled with sea water or with a salt solution having

the same conductivity, and the open 'upper cell' with a measured amount of a solution of the same salt as that in the lower cell but of one-half the concentration. The rate of increase in the conductivity of the solution in the upper cell served as a measure of the rate of passage of salts through the tissues, and hence of the permeability of the tissue to that salt. The errors due to diffusion of salts from the tissue, to individual differences in the age and thickness of the fronds, and to variations in the area of tissue through which salt could pass, were eliminated by suitable controls.

The effect of the intercellular material was determined by experiments in which dead tissue took the place of living. The outcome of these experiments was independent of the method of killing. Sodium

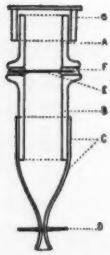

FIG. 1.

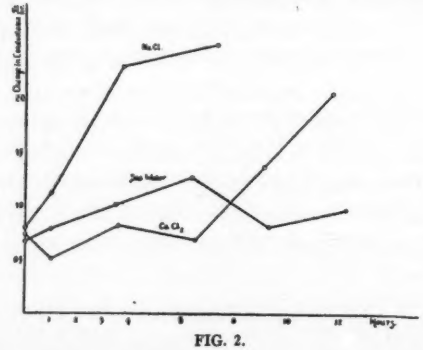

FIG. 2.

FIG. 1. APPARATUS FOR THE DETERMINATION OF PERMEABILITY BY DIFFUSION THROUGH A DIAPHRAGM OF TISSUE.

FIG. 2. PROGRESSIVE CHANGES IN THE PERMEABILITY OF *LAMINARIA* TISSUE CAUSED BY SOLUTIONS OF DIFFERENT SALTS.

and calcium chlorides, lanthanum nitrate and the salts of sea water passed through the diaphragm of dead tissue at a very considerable rate which did not differ materially in the case of the different salts; the rate of change of conductivity of the solution in the upper cells was between 2.1% and 2.2% per hour during successive four and one-half hour periods of diffusion of the different salts through the tissue. There was therefor no selective permeability of the intercellular substance to the ions used, and no alteration of its permeability caused by these salts.

Table 1, based on experiments with living tissue, shows that the rate of diffusion of different salts through the protoplasm was considerable, and that it was greatly increased by sodium chloride in pure solution; that it remained nearly normal in sea water (the increase in the rate of

diffusion of the salts of sea water in the later periods of an experiment was apparently due to injury of the protoplasm by unfavorable conditions necessarily imposed by the experiment), and that it was decreased considerably by calcium chloride and still more by lanthanum titrate.

Figure 2 shows that the decrease in permeability due to calcium chloride, is temporary. It is succeeded by an increase of permeability, which in the case of calcium chloride (as well as in the case of sodium chloride, which produces an immediate increase), culminates in a rate of diffusion which is the same as that through killed tissue.

These experiments show that the protoplasm of *Laminaria* is permeable to inorganic salts, and that characteristic alterations in its permeability are produced by various salts. Sodium chloride causes an

TABLE 1

PERMEABILITY OF LIVING *Laminaria*

EXPERIMENT NUMBER	UPPER SOLUTION	FIRST PERIOD			SECOND PERIOD				RATIO 2D PERIOD / 1ST PERIOD
		Lower solution	Duration h. m.	Change per cent per hour	Upper solution	Lower solution	Duration h. m.	Change per cent per hour	
18	½ sea water	sea water	2.05	0.73	½ sea water	sea water	2.00	0.78	1.07
19	½ sea water	sea water	2.00	0.79	NaCl 0.26 M	NaCl 0.52 M	2.00	1.11	1.41
22	½ sea water	sea water	2.04	0.73	$CaCl_2$ 0.14 M	$CaCl_2$ 0.28 M	2.02	0.51	0.70
17a	½ sea water	sea water	1.35	0.73	$La_2(NO_3)_6$ 0.05 M	$La_2(NO_3)_6$ 0.10 M	1.35	0.33	0.45

increase in permeability culminating in death. Calcium chloride causes a temporary decrease in permeability, followed by an increase, culminating in death. Certain preliminary experiments indicate that the great decrease in permeability produced by lanthanum nitrate is followed by an increase, presumably culminating in death.

It was possible to demonstrate by suitable modifications of the diffusion methods, described above, that the cell walls of the epidermis from the inner surface of the bulb scales of the onion are exceedingly impermeable to sodium, calcium and aluminium chlorides, sodium hydroxide, eosin and Bordeaux red, and slightly permeable to hydrochloric acid.

2. The observations of many investigators are best explained on the assumption that when cells in equilibrium with the liquid normally fill-

ing the intercellular spaces come into contact with a dilute solution which replaces the intercellular sap, a disturbance of equilibrium occurs, involving loss of solutes from the cell. Such an 'exosmosis' would delay the recovery of a plasmolysed cell.

The comparative rate of exomosis of electrolytes was studied in strips of the peduncles of the common dandelion (*Taraxacum officinale Weber*) and was determined in the following manner: comparable lots of tissue were placed for a period of twenty minutes in isotonic solutions of sodium, calcium and aluminium chlorides, and in an isotonic balanced solution containing salts in the following molecular proportions: NaCl 68.4%, $CaCl_2$ 19.8%, $MgCl_2$ 6.7%, $MgSO_4$ 3.3% and KCl 1.9%, and in distilled water. After removal from these solutions the lots of tissue were rinsed and placed in measured amounts of distilled water, whose conductivity was determined at suitable intervals. It had previously been determined that outward diffusion of the salts which had entered the tissue from these solutions was practically complete in thirty minutes. After thirty minutes the rate of change of conductivity of the distilled water bathing the tissue was therefor a measure of the rate of exosmosis of electrolytes normally present in the cell.

The rate of exosmosis from tissue previously exposed to distilled water or to the balanced solution was less than that from tissue treated with sodium chloride, and greater than that from tissue treated with calcium chloride. The tissue treated with cerium chloride showed a slow exosmosis which after a time became quite rapid, ultimately exceeding that from any other lot of tissue. This effect was probably due to the toxic effect of the cerium, which, like lanthanum, causes an increase of permeability following the initial decrease. The data are graphically presented in figures 3 and 4.

It is therefore apparent that exosmosis from living cells is influenced by salts such as are frequently used in plasmolytic experiments. In *Taraxacum*, as in *Laminaria*, sodium increases permeability, while calcium cerium and lanthanum cause an initial decrease. A balanced solution may be prepared, of a constitution such that it will cause no appreciable alteration in the permeability of the protoplasm of a given plant.

3. The conclusions derived from the experiments on exosmosis were were confirmed and amplified by experiments in which changes in turgidity were used to measure the rate of penetration of sodium potassium, calcium, magnesium, aluminium and cerium chlorides, potassium nitrate, saccharose, and the balanced solution heretofore described.

Strips of peduncle were fastened at one end in a horizontal position in a suitable dish, and in such a manner that the free end moved horizontally as the curvature of the strip changed in response to changes in its turgidity. The movement of the free end was then observed by means of a microscope. The strips were first allowed to come into osmotic equilibrium with a solution originally very nearly isotonic with the cells. A slight increase in concentration was then made, and the time required by the strip to return to its original position after the loss of curvature thus caused, was noted. Immediately upon the recovery of a strip, the concentration of the solution bathing it was again increased,

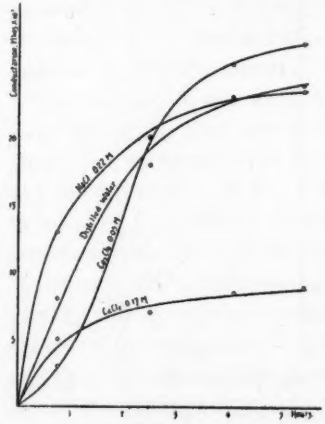

FIG. 3.

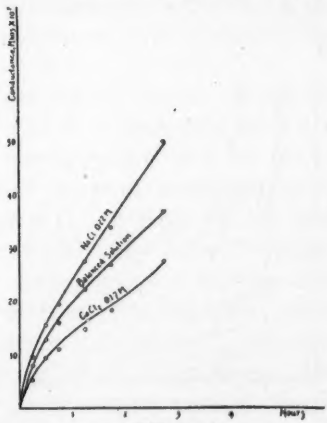

FIG. 4.

FIG. 3. THE EFFECT OF PREVIOUS TREATMENT OF PEDUNCLES OF *TARAXACUM* WITH SOLUTIONS OF DIFFERENT SALTS ON THE CONDUCTIVITY OF DISTILLED WATER IN CONTACT WITH THE TREATED TISSUE.

FIG. 4. THE EFFECT OF PREVIOUS TREATMENT OF PEDUNCLES OF *TARAXACUM* WITH PURE AND BALANCED SALT SOLUTIONS, ON THE CONDUCTIVITY OF DISTILLED WATER IN CONTACT WITH THE TREATED TISSUE.

and the 'recovery time' again noted. In this manner a series of 'recovery times' of the same strip was obtained. In the absence of exosmosis the molecular increase in concentration, divided by the 'recovery time' affords an empirical measure of the rate of penetration of the plasmolysing substance.

The data graphically presented in figures 5 and 6, show that the rate of recovery was increased by the salts of the monovalent kations, and by saccharose, while in the salts of bi- and trivalent kations it was less than that in the balanced solution. The first group exhibits also a characteristic secondary decrease in the rate of recovery which may be due to exosmosis from the cells.

It will be seen that these observations are in accord with those made by other methods; and in addition it shows the advantage of a balanced solution over saccharose (which is often used on the assumption that it does not penetrate nor alter the permeability of protoplasm) in experiments in which it is desirable to maintain the normal permeability of living cells.

Summary.—Determinations of permeability have been made by a new method, which is independent of other methods, as well as by improved forms of existing methods.

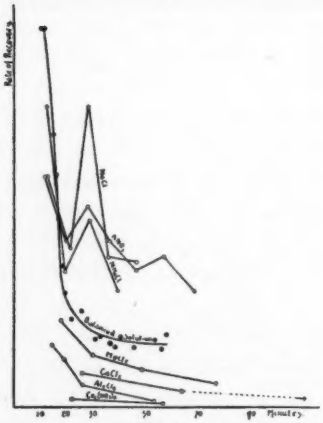

FIG. 5.

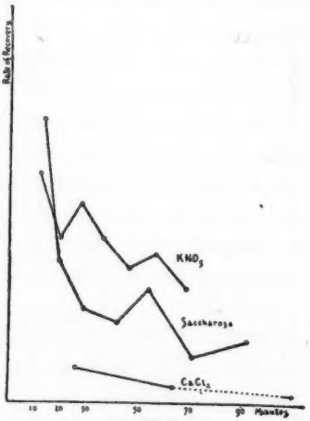

FIG. 6.

FIG. 5. THE RATE OF PENETRATION OF SALTS IN PURE AND BALANCED SOLUTION INTO LIVING CELLS OF *TARAXACUM*.

FIG. 6. THE RATE OF PENETRATION OF SACCHAROSE AND OF SALTS IN PURE SOLUTION INTO LIVING CELLS OF *TARAXACUM*.

The results agree in showing:

(1) That living protoplasm is normally permeable to the salts studied.

(2) That salts in pure solution may alter permeability, some (like sodium chloride) causing an increase of permeability while others (like calcium, lanthanum and cerium chlorides) cause a decrease, followed by an increase, of permeability.

(3) In a properly balanced solution the permeabilit remains normal.

(4) Cell walls may be semipermeable to an extent which renders them important in such experiments.

POINT SETS AND CREMONA GROUPS. PART III

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In Part I[1] of this series projectively distinct sets P_n^k of n points in S_k were mapped upon points of a space $\Sigma_{k(n-k-2)}$ and a certain Cremona group $G_{n!}$ in Σ was obtained by permutation of the points of the set. In Part II[2] the G_n appeared as merely a subgroup of a more important group $G_{n,\,k}$ in $\Sigma_{\,k(n-k-2)}$ which also is defined by P_n^k. In particular the G_6, in Σ_4 attached to P_6^2 is a subgroup of the $G_{6,\,2}$ in Σ_4 which has the order 51840 and is isomorphic with the group of the lines on a cubic surface.

The purpose of this Part III is to utilize the $G_{6,\,2}$ in the problem of determining the lines of a cubic surface C^3. It appears that there is a one-to-one correspondence between the invariants of C^3 and the invariant spreads of $G_{6,\,2}$ in Σ_4. The lines of C^3 can be rationally expressed in terms of a solution of the form problem of $G_{6,\,2}$ by means of a typical representation of C^3 in the hexahedral form with the aid of the linear covariants of C^3. In order to solve the form problem of $G_{6,\,2}$ the simplest linear system of irrational invariants of C^3 is employed. This system is of dimension 9 and the members appear in Σ_4 as quintic spreads. Under the invariant subgroup $\Gamma_{6,\,2}$ of $G_{6,\,2}$ of index two this linear system separates into two skew linear systems each of dimension 4 with the important property that the members of the two systems are permuted under the operations of $G_{6,\,2}$ precisely as the points and S_3's of a linear space S_4 are permuted under the elements of a correlation group in S_4 whose collineation subgroup is the Burkhardt group G_{25920} in S_4. The form problem of $G_{6,\,2}$ can then be solved in terms of a solution of the form problem of G_{25920} by using the point invariants of G_{25920} and in addition five invariants of G_{25920} linear in the S_3 coördinates and of degrees 1, 7, 9, 13, 15 in the point coördinates.

The method for solving the form problem of G_{25920} is suggested by the properties of the normal hyperelliptic surface M_2^{18} of grade 3 in S_8 obtained parametrically by using 9 linearly independent theta functions of the third order and zero characteristic. The M_2^{18} admits a collineation group $G_{2,\,81}$ which contains 81 involutions. If I is one of these involutions the fixed S_3 and fixed S_4 of I meet M_2^{18} in 6 and 10 points respectively. The M_2^{18} is projected from the fixed S_4 upon the fixed S_3 into a doubly covered Weddle surface and from the fixed S_3 upon the fixed S_4 into a doubly covered 2-way N_2^6 which has a node

at α. If N_2^6 be projected from α it becomes a Kummer surface. There is a family of ∞^3 surfaces M_2^{18} with the same $G_{2\cdot 81}$. By projection we obtain a family of N_2^6's whose node α runs over a quartic spread J_4—the simplest invariant of G_{25920}. The 10 points in the S_4 of I run over the Hessian J_{10} of J_4. The spread J_4 is its own Steinerian and the polar cubic of a point α on J_4 as to J_4 is a Segre cubic spread with nodes at the 10 points on J_{10}, and of course a simple point at α. The point α on its polar cubic determines a binary sextic—the fundamental sextic of the hyperelliptic funetions. In this way the solution of the form problem of G_{25920} in terms of hyperelliptic modular functions becomes apparent at once *in the special case* when $J_4 = 0$. This restriction is removed later by a conventional method. The conclusions above all are drawn from the existence of a set of 9 quadrics whose complete intersection is the normal spread M_2^{18} and whose coefficients are the modular forms α.

The above determination of the lines of C^3 differs from that of Klein[3] in that no equation of degree 27 or other resolvent equation is employed. All the processes are effected within the domain of the invariants and linear covariants of C^3. Klein also uses as fundamental form problem that of the Maschke collineation group in S_3 rather than the Burkhardt form problem. This implies the isolation of a root of the underlying binary sextic. The accessory irrationalities required are thereby somewhat simpler.

[1] These PROCEEDINGS, **1**, 245 (1915); *Trans. Amer. Math. Soc.*, **16**, 155 (1915). This series of investigations has been pursued under the auspices of the Carnegie Institution of Washington, D. C.

[2] These PROCEEDINGS, **2**, 244 (1916); *Trans. Amer. Math. Soc.*, **17**, 345 (1916).

[3] That an equation of degree 27 for the lines of a cubic surface could be solved by hyperelliptic modular functions was first pointed out by Klein, *J. Math., Paris*, Ser. **4**, **4**, 169 (1888). His suggestions were elaborated by Witting, *Math. Ann., Leipzig*, **29**, 167 (1887); by Maschke, *Ibid.*, **33**, 317 (1889); and by Burkhardt, *Ibid.*, **35**, 198 (1890), **38**, 161 (1891), **41**, 313 (1893).

THE INTERFERENCES OF SPECTRA BOTH REVERSED AND INVERTED

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This is an interesting combination of the two methods of investigation hitherto given (Carnegie Publications, No. 249, 1916, §4) and not very difficult to produce. Retaining the adjustment for inverted spectra

the white light impinging on the grating is previously dispersed, preferably by an Ives direct vision grating (with auxiliary prism). The rulings of both gratings (the Ives grating being between the collimator, at some distance, and the first grating of the interferometer) are to be parallel. If the grating constants D_1 are different ($D = 167 \times 10^{-6}$ cm. film, and $D = 352 \times 10^{-6}$ cm. ruled grating, were employed) the spectra in the telescope are naturally of different lengths: for the dispersion of the Ives grating is increased on one side and decreased on the other side, by the grating of the interferometer. Moreover this decrease from the larger dispersion of the first grating is beyond zero (achromatism) into negative values. Hence the corresponding duplicate spectrum in the telescope is a small spectrum with a large spectrum reversed relatively to it, while the inversion remains intact. In the experiment made, the larger doublet, $D'_1\ D'_2$, was somewhat more than twice as broad as the smaller $D_1\ D_2$.

It is now merely necessary to place any longitudinal axis (line of symmetry) of the two spectra seen in the telescope in contact; or it is but necessary that the spectra are longitudinally parallel and overlap. The phenomenon then appears at the intersection of the lines of longitudinal and of transverse symmetry. It is thus proportionately nearer the smaller $D_1\ D_2$ and farther from the larger $D'\ D'$ doublets, but always between them. If the $D_1\ D_2$ lie within the $D'_1\ D'_2$ lines, the fringes lie within the $D_1\ D_2$ pair.

The phenomenon which should be observed with a powerful telescope, usually consists of three or fewer small elongated dots, lying within an elliptic locus, the locus usually having a transverse axis (parallel to the Fraunhofer lines) about two or three times as long as the longitudinal axis (parallel to lengths of spectra). Usually the width was $D_1\ D_2$ and the length larger than $D'_1\ D'_2$, but this ratio may be changed by screening off the wavefront. The fringes were not more than one-half of $D_1\ D_2$ apart.

The interesting result is here again met, incidentally, that spectra from the same white source, though of different lengths, are nevertheless quite capable of producing strong interferences on overlapping.

In further experiments with the long collimator and very bright spectra, a variety of other forms was obtained. In most patterns the elliptic outline, sometimes circular, is always evident from the enhanced brightness of the bright fringes of the spot. As any adjustment of overlapping spectra suffices, the D lines may be quite out of the field, or the spectra may be slightly separated with the interference spot in the gap.

The experiment was also made of crossing the spectra at some other angle than 0° or 180°. For instance, the rulings of the Ives grating were placed at right angles to those of the interferometer grating, as in Newton's method of crossed prisms. Seen in the telescope (adjusted for inverted spectra) the two spectra now made an elbow with each other, while the $D_1 D_2$ lines were still parallel and could be put in coincidence. On using a long (meter) collimator, strong interferences were obtained in the line of symmetry of the elbow and normal to the D lines. They have the same characteristics as the preceding and persist during a displacement of mirror of about 0.3 cm.

SEX INTERGRADES IN A SPECIES OF CRUSTACEA

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In unisexual forms we are accustomed to think of the term male as signifying the possession by the animal indicated not only of a sperm-producing organ and the associated accessory male reproductive structures but also of certain definite secondary sex characters, definite characters of form and structure and, further, of conspicuous physiological and psychological characteristics. The term female implies definite and marked characters contrasting with those of a male on all these points. In other words maleness and femaleness are generally taken to indicate definite and precise opposed and alternative states, only one of which may obtain in a single individual.

The occurrence of known deviations from the conditions of maleness and femaleness are in the main confined to a comparatively few isolated and sporadic cases of hermaphroditism and gynandromorphism. Gynandromorphs are really sex mosaics inasmuch as a definite portion of the body, frequently one-half, possesses *in toto* the definite characters of one sex and the remainder of the body is distinctively of the other sex. However two workers have published concerning stocks in which considerable numbers of individuals are intermediate in their sexuality—intermediate not as sexual mosaics but quantitatively and as a whole different from either the normal male or the normal female. Riddle[1] has demonstrated intermediate sex forms in his pigeons and Goldschmidt has obtained such forms in the offspring of certain crosses in the gypsy moth.

In a species of crustacean the writer has obtained intermediate sex forms (for which the term *sex intergrade* seems appropriate) constitut-

ing a large percentage of the population. The significance of this material may better be considered after some acquaintance with it.

About four years ago two lines of a species of small phyllopod crustacean, *Simocephalus vetulus*, were taken from outdoor ponds, and their propagation continued in the laboratory. Throughout the experiment young have been isolated in individual bottles when not more than a day old. They reproduce parthenogenetically beginning when seven to twelve days of age, the first brood ordinarily containing from 8 to 20 young.

In addition to numerous other lines of this and other species of Cladocera, six separate strains of one line, '740,' have been propagated. For 130 generations these six strains (like all the other strains of Simocephalus to date) produced nothing but parthenogenetic females. Several lines of each of four other species of Cladocera have been propagated for long periods of time in the same manner as Simocephalus and except for a few males in one of the many lines they have produced only females.

But last October in the 131st generation of one of the strains of line 740 there suddenly appeared a large percentage of males together with normal females and a large number of sex intergrades—males with one or more female secondary sex characters, females with one to several male characters and some hermaphrodites with various combinations of male and female secondary sex characters.

At this point we may consider the criteria of sex in this species. The character of the sex gland,—whether a testis or an ovary—is readily determined by microscopic observation of the living animal. In addition, eight secondary sex characters distinguish the female from the male sex: (1) *body size*, the females rapidly outstrip the males in growth and are considerably larger at sexual maturity; (2) *size and position of eye*, the eye in the female is smaller than in the male and does not crowd the margin of the head as in the male; (3) *outline of the head*, the antero-ventral margin of the head is less angulated in the female than in the male; (4) *absence of the nuchal protuberance*, there is a slight dorsal protuberance immediately anterior to the cervical suture, typically in the male only; (5) and (6) *character of the first (rudimentary) antennae*, in the female the basal portion of the antenna is not enlarged and bears a single lateral spine (or stylet), whereas in the male the swollen condition of the basal portion of the antenna and the presence of two lateral stylets are distinctive. Since the two antennae in the same individual frequently are unlike, the character of each antenna counts as a separate diagnostic character;

(7) and (8) *outline and armature of the lateral post-abdomen margins,* in the female these margins are decidedly concave and bear posteriorly no teeth or only rudimentary 'teeth.' In the male the margin is slightly or not at all concave and bears larger teeth which also extend posteriorly much farther than in the female. Since the two post-abdominal margins often differ in character the nature of each margin constitutes a diagnostic sex character.

That these eight characters are really diagnostic secondary sex characters for the female is indicated by the fact that they occur in all individuals in the lines of Simocephalus which are reproducing parthenogenetically in the usual fashion, i.e., producing nothing but females. Again in a derived strain, in which for a time there appeared both females and males, but no sex intergrades, each female and male possessed all the secondary sex characters indicated above for its sex.

The sex intergrades are of almost all possible sorts from females with a single male secondary character to females with all eight of the secondary characters male, hermaphrodites with many combinations of secondary sex characters, and, finally males with one to several (never as many as eight, however) female characters.

The highly male-like female intergrades produce few young. Not infrequently they are entirely sterile. A female intergrade with as many as six strong male secondary characters rarely produces young. Many female intergrades with fewer than six male secondary sex characters are likewise sterile. In most of the sterile individuals eggs are produced but either they fail to develop after passing into the brood pouch or, more generally, the ovarian development is not completed and the eggs disintegrate in the ovary. To cite illustrative cases: two female intergrades in the 132d generation each had five male characters and though eggs began to form, the ovarian development was not completed and no eggs ever appeared in the brood pouch. A sibling of these had only the antennae male in character yet produced only a single brood. This case however is rather unusual as such individuals are usually quite prolific. In the 133d generation a female intergrade with four male secondary characters produced three broods consisting in all of only 15 individuals. On the other hand some individuals with several secondary male characters prove to be very prolific. A sibling of the last-mentioned individual had five secondary male characters and in addition one side of its post-abdomen was somewhat male in character yet it had a high prolificacy. In general in addition to being more prolific one may say that female intergrades with few o less distinctly male characters produce a smaller percentage of males and

sex intergrades than those having a larger number or more definitely male characters.

Males that bear one or more female secondary sex characters in nearly every case have incompletely developed reproductive systems—one or both testes, though filled with sperm, being shorter than normal or lacking all or part of the sperm duct. In most cases the entire sperm duct is lacking. Some males, normal in their secondary sex characters, have similar incomplete reproductive systems.

By propagating from female intergrades we are able to continue the production of mixed broods—females, males and sex intergrades. This has now continued for 16 generations with no apparent change in the ratio of the various sex forms and with no apparent tendency of the stock to lose vigor or become less prolific.

From the sex intergrade stock we have derived in its third generation (the 133d generation under laboratory conditions) a normal strain producing nothing but typical females.

The origin of this all-female-producing strain is of interest. An almost sterile hermaphroditic intergrade produced only two young. One of these offspring was a female intergrade. This individual produced 202 young, 2 of which were normal females, 16 were female intergrades, 4 were hermaphrodites, 12 were male intergrades and 67 were normal males. In addition 3 individuals were not examined while 10 females (including female intergrades) and 88 males (including male intergrades) were undescribed. Probably only two individuals (1% of the whole), from the entire number of offspring from this individual were normal females. The only sibling of this female intergrade was a normal female which produced nothing but typical females, and from this individual came a derived normal strain which has now descended for 23 generations in the usual fashion without reversion to the production of sex intergrades. For two generations, however (the 13th and 14th from its origin from the sex intergrade strain), this derived strain did produce a considerable percentage of males. These males were all normal however and their sisters were all normal females, there being no return to the production of sex intergrades as in the parent stock. Following these two generations, in which males were produced, this derived strain has produced nothing but normal females in the nine generations which have occurred to date (August 10). From the 11th generation of the sex intergrade strain a second normal strain producing only typical females has been derived. More recently two additional normal all-female-producing strains have appeared.

As suggested above the various mothers in the sex intergrade strain differ markedly in the proportion of normal sex forms and sex intergrades while they produce. For example, for a given mother the percentage of males—normal males and definitely male intergrades of all grades—varies from 8 or 10% to 100%, the more usual figures being 45 to 85%. The percentages from the same mother from brood to brood vary of course but the sex array and its proportion in the first brood provide a basis for an estimate of what is to be expected in future broods.

The main interest in this material would seem to lie in the remarkable array of sex forms, the stock in general consisting of perhaps 40% normal males and about 8% normal females, the remainder being intergrades with *almost* every combination of male and female secondary and primary sex characters. More than half the individuals are neither wholly male nor wholly female but possess definite morphological sex characters of both sexes. The writer has attempted to classify these individuals on the basis of sex characters into more than twenty classes or grades. A grade at one end of the scale contains normal females; at the other end of the scale there is a class of normal males. Between these extreme grades are others for the many types of sex intergrades. Even this large number of grades is scarcely sufficient; many individuals occur which are intermediate between these grades and can with difficulty be assigned to any of them.

Sex here reveals itself not as a fixed and definite state but as a purely relative thing. No arbitrary classification into males and females is justifiable or possible; not only because of the confusing admixture of male and female secondary sex characters but also because the same individual, even the same sex gland, may develop eggs and sperm at the same time or sperm at one time and eggs at another time.

It seems probable that in this species sex depends upon a number of elements (I believe them to be largely or exclusively environmental factors) which influence the general physiological whole. In the stock which produces the sex intergrades the more usual association and the culmination of these influences has become interrupted. There is a consequent abnormal physiological balance resulting in haphazard combinations of sex-characters and a shifting of the balance one way or the other. Sometimes the result is a balance so unstable that in certain cases it seems to be shifted within a few days in the same individual or within portions of that individual as indicated by changes in the sex products.

Of secondary interest is the method of origin of the sex intergrade

strain. The usual sex balance has become disturbed. The cause or method of this disturbance is not definitely known. But whatever the cause, the disturbance influenced not only the individual but also its germ plasm and the disturbed balance is evident throughout succeeding generations. The origin of this disturbance of the sexual balance may be referred to as a mutation. While there is little evidence concerning its cause, there seems abundant evidence concerning its permanent character so far as this strain is concerned.

The derivation from this sex intergrade strain of several strains which produce only *normal* (so far as may be judged by their morphological characters at any rate) females, and, on occasion, *normal* males, is a phenomenon similar to that of the sudden appearance of the sex intergrade strain and might with equal propriety be called a return mutation.

I am inclined to believe from evidence from many Cladocera, and from other forms reproducing parthenogenetically during most of the time and by means of sexual reproduction at irregular and uncertain intervals, that environmental factors in all such forms wield the determining influence. The evidence at hand in the present case, however, is not very conclusive and must be reserved for the larger paper.

[1] The following references may be cited:

Goldschmidt, R., Erblichkeitsstudien an Schmetterlingen. I, *Zs. ind. Abs.—Vererbungslehre*, **7**, 1–62 (1912); and a preliminary report on further experiments in inheritance and determination of sex, these PROCEEDINGS, **2**, 53–58.

Riddle, Oscar, Statement run in the *Carnegie Inst. Washington Year Book*, **12**, 322 (1913); and Sex control and known correlations in pigeons, *Amer. Nat.*, **50**, 385–410 (1916).

SOME PROBLEMS OF DIOPHANTINE APPROXIMATION: A REMARKABLE TRIGONOMETRICAL SERIES

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1. The title of this note is perhaps not very appropriate: we retain it because the contents of the note form a natural sequel to those of three papers which we have published under same title elsewhere,[1] and in particular those of our second paper in the *Acta Mathematica*. We there discussed in detail the series

$$\sum e^{\alpha\pi i n^2 + 2\theta\pi i n}, \tag{1.1}$$

and other similar series associated with the elliptic Theta-functions, and used our results to elucidate a variety of difficult points in the theory

of Taylor's series and trigonometrical series. We have since discovered that even simpler and more elegant illustrations may be derived from the series

$$\sum e^{\alpha\pi i n \log n + 2\theta\pi i n}. \tag{1.2}$$

This series behaves, for different values of the parameters α and θ, far more regularly than does the series (1.1). To put the matter roughly, the behaviour of the series *does not, in its most essential features, depend upon the arithmetic nature of* α.

2. Our fundamental formula is

$$\sum_0^\infty a^{\rho n} e^{-ya^n} = \frac{1}{\log a} \sum_{-\infty}^{\infty} \Gamma\left(\rho + \frac{2\pi i n}{\log a}\right) y^{-\rho - \frac{2\pi i n}{\log a}} - \sum_0^\infty \frac{(-y)^n}{n!\,(a^{\rho+n}-1)}. \tag{2.1}$$

Here $a > 1$, ρ is real, and $\mathsf{R}(y) > 0$. The formula becomes illusory when ρ is zero or a negative integer, but the alterations required are of a trivial character. The formula is easily proved by means of Cauchy's Theorem: similar formulae were proved by one of us in a paper published in 1907.[2]

We now write $y = \sigma + it$, where $t > 0$, suppose that $\sigma \to 0$, and approximate to the series of Gamma-functions by means of Stirling's Theorem. We thus obtain

$$\frac{Ht^{-\rho}}{\log a} e^{-\frac{1}{2}\pi i} f(z) = F(\sigma) + \phi(\sigma), \tag{2.2}$$

where

$$f(z) = \sum_1^\infty n^{\rho-\frac{1}{2}} e^{\alpha i n \log n} z^n; \tag{2.21}$$

$$\alpha = \frac{2\pi}{\log a}, H = \frac{(2\pi)^\rho}{(\log a)^{\rho+\frac{1}{2}}}, z = re^{i\theta}, r = e^{-\alpha\sigma/t}, \theta = \alpha \log\left(\frac{\alpha}{et}\right), \tag{2.22}$$

so that $r \to 1$ when $\to \sigma\ 0$;

$$F(\sigma) = \sum_0^\infty a^{\rho n} e^{-(\sigma+it)a^n}; \tag{2.23}$$

and $\phi(\sigma)$ is of one or other of the forms

$$A + o(1), O\left(\log\frac{1}{\rho}\right), O(\sigma^{-\rho+\frac{1}{2}}),$$

according as $\rho < \frac{1}{2}$, $\rho = \frac{1}{2}$, or $\rho > \frac{1}{2}$.

3. It is known[3] that, if $\rho > 0$,

$$F(\sigma) = O(\sigma^{-\rho}), F(\sigma) = \Omega(\sigma^{-\rho}), \tag{3.1}$$

when $\sigma \to 0$, the second of these formulae meaning[4] that $F(\sigma)$ is *not* of the form $o(\sigma^{-\rho})$, and the two together that

$$0 < h = \overline{\lim}\, \sigma^{\rho} F(\sigma) < \infty. \tag{3.2}$$

These relations all hold uniformly in t. It follows that, if $\rho > 0$ and $r = |z| \to 1$, *the function* $f(z)$ *is exactly of the order* $(1-r)^{-\rho}$, *and this uniformly in* θ. Incidentally, of course, it follows that every point of the unit circle is a singular point: but this is known already.[5]

The series furnishes an example in which the orders in the unit circle of the functions $f(z) = \Sigma a_n z^n$ and $g(z) = \Sigma |a_n| z^n$ differ by exactly $\frac{1}{2}$, the maximum possible.[6]

When $\rho = 0$, $f(z)$ is bounded, but does not tend to a limit when z approaches any point of the unit circle along a radius vector. We know of no other example of a function possessing this property. When $\rho < 0$, $f(z)$ is continuous for $|z| \leq 1$.

4. Let

$$s_n = \sum_1^n k^{\rho - \frac{1}{2}} e^{\alpha i k \log k + 2\theta \pi i k}, \tag{4.1}$$

and suppose first that $\rho > 0$. Then it is easy to deduce from the results of §3 that s_n is of the form $\Omega(n^{\rho})$ when $n \to \infty$. The corresponding 'O' result lies a little deeper: all that can be proved in this manner is[7] that $s_n = O(n^{\rho} \log n)$. But a direct investigation, modelled on that of the early part of our second paper in the *Acta Mathematica*, shows that the factor $\log n$ may be omitted. It should be observed that an essential step in our argument depends on an important lemma due to Landau,[8] according to which

$$\left| \int_1^X x^{\gamma} e^{ix \log (\eta x)}\, dx \right| < 23 X^{\gamma + \frac{1}{2}} \tag{4.2}$$

for $X \geq 1$, $\gamma \geq 0$, $\eta > 0$. We thus find that s_n *is, for every positive value of* α, *exactly of the order* n^{ρ}, *and this uniformly in* θ. *The series*

$$\sum n^{\rho - \frac{1}{2}} e^{\alpha i n \log n + 2\theta \pi i n} \tag{4.3}$$

is never convergent, or summable by any of Cesàro's means.

When $\rho = 0$, s_n is bounded, but the series is never convergent or summable. When $\rho < 0$ it is convergent; and uniformly in θ.

5. For further applications it is necessary to consider the real and imaginary parts of our function and series separately, and this is most easily effected by introducing some restriction as to the value of α. Suppose that a is an integer, not of the form $4k+1$. Thus we may take $a = 2$, $\alpha = 2\pi / \log 2$. Then the results of §§3–4 hold for the real and

imaginary parts of the function or the series. In particular *the series*

$$\sum n^{\rho-1} \cos(\alpha n \log n + 2\theta\pi n) \quad (\rho \geq 0) \tag{5.1}$$

is never convergent or summable for any value of θ, and is accordingly not a Fourier's series. We thus obtain a solution of what, in our former paper, we call Fatou's[9] problem which combines all the advantages of those given previously by Lusin,[9] Steinhaus,[9] and ourselves.

We can also obtain in this manner exceedingly elegant examples of continuous non-differentiable functions. Thus *the function*

$$f(\theta) = \sum \frac{\sin(\alpha n \log n + 2\theta\pi n)}{n^{\beta}} \quad (1 < \beta \leq \tfrac{3}{2}) \tag{5.2}$$

does not possess a finite differential coefficient for any value of θ.

[1] G. H. Hardy and J. E. Littlewood, Some problems of Diophantine approximation (i) *Proc. Fifth Int. Congress Math.*, Cambridge, **1**, 223–229 (1912); (ii) *Acta Math.*, **37**, 155–190 (1914); (iii) *Ibid.*, 193–238.

[2] G. H. Hardy, On certain oscillating series, *Quarterly J. Math.*, **38**, 269–288 (1907).

[3] G. H. Hardy, Weierstrass's non-differentiable function, *Trans. Amer. Math. Soc.*, **17**, 301–325, (1916).

[4] *l. c. supra* (1) (iii), p. 225.

[5] G. N. Watson, The singularities of functions defined by Taylor's series, *Quarterly J. Math.*, **42**, 41–53 (1911).

[6] G. H. Hardy: (i) A theorem concerning Taylor's series, *Ibid.*, **44**, 147–160 (1913); (ii) Note in addition to a theorem on Taylor's series, *Ibid.*, **45**, 77–84 (1914).

[7] Cf. E. Landau, Abschätzung der Koeffizientensumme einer Potenzreihe: (i) *Arch. Math. Physik*, ser. 3, **21**, 42–50 (1913); (ii) *Ibid.*, 250–255; (iii) *Ibid.*, **24**, 250–260 (1915).

[8] E. Landau, Uber die Anzahl der Gitterpunkte in gewissen Bereichen, *Göttinger Nachrichten*, 687–771 (p. 707), (1912).

[9] For references see p. 232 of our paper (1) (iii).

STERIC HINDRANCE AND THE EXISTENCE OF ODD MOLECULES (FREE RADICALS)

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The discovery of certain unpredicted facts in organic chemistry has led to the employment of the elusive phrase 'steric hindrance,' a phrase, however, which seems too vague in its significance to connote a real scientific theory. If a steric influence upon a chemical reaction be defined as one which is due to the room occupied by a large atom or group of atoms, such a definition leaves an opportunity for that kind of confusion, which is too frequently found in chemical literature, between

the factors that determine the speed of a reaction and those that determine the conditions of final equilibrium. In order to avoid such confusion it is necessary to distinguish between two possible types of steric influence:

1. A group of atoms, owing to its size and to its position in a molecule, may stand in the way so as to impede a reaction in which that molecule is involved. In other words, it may act merely to diminish the speed of such a reaction.

2. The space about a given atom may be so completely occupied by certain large groups of atoms, before the natural valence of the central atom is satisfied, that the entrance of another large group will be prevented; or if such a group occasionally enter, it will again be forced out through lack of room.

I think it will be admitted that these ideas, plausible as they are, should not be introduced into the already very complex body of chemical theory until phenomena are known which cannot be so well explained in other ways. In this paper I wish to discuss the so-called free radicals of organic chemistry, in the interpretation of which the term 'steric hindrance' has so often been employed, and to show that, in this case at least, another explanation can be offered which is more satisfactory in that it correlates a larger number of known phenomena.

After Gomberg, by treating triphenylmethyl chloride with metals, obtained a substance which he believed to contain triphenylmethyl, thus giving rise to one of the most interesting chapters of modern organic chemistry, it was at first commonly believed that by some other method a hexaphenylethane might be produced which would be stable and unreactive, and which would be formed from triphenylmethyl except for the retardation of this reaction by the first type of steric hindrance which I have just defined. We are now convinced that this is not the case. The later work of numerous investigators, which has been very completely reviewed by Gomberg[1] in his interesting summary, 'The Existence of Free Radicals,' has satisfactorily cleared an extremely intricate situation. A careful study of the work of these authors must, I believe, lead to the acceptance of the following perfectly definite conclusions concerning the class of hexa-arylethanes, of which hexaphenylethane is the simplest example.

I. The hexa-arylethanes, aside from the irreversible processes of intramolecular rearrangement and autoxidation to which they are subject and which we shall not further consider, exist in a state of tautomeric equilibrium between quinoid forms and the benzoid form which represents the simple substituted ethane. As in most similar cases the

equilibrium is shifted in favor of the quinoid type in polar solvents, and in a very polar solvent such as SO_2 the molecules may dissociate into positive and negative ions of which the former (and probably the latter also) is largely in the quinoid form.

The recognition of the existence of the quinoid form is indispensable to an understanding of numerous reactions which characterize the hexaarylethanes, but since we are here concerned with that part of the substance which remains in the benzoid form we may proceed at once to the next conclusion.

II. In nonpolar solvents such as benzene the substituted ethanes exist chiefly in the benzoid form and are to a greater or less extent dissociated into the triarylmethyls. The undissociated part is colorless. The product of dissociation, though colored, has also the benzoid form.

The fact of dissociation has been abundantly demonstrated. The mere fact that the equilibrium between colorless and colored forms changes in favor of the latter with increasing dilution[2] shows that the change from colorless to colored is attended by an increase in the number of molecules. Measurements of the degree of dissociation, whether through molecular weight determinations or by colorimetric methods, show that while the parent substance, hexaphenylethane, is at ordinary temperatures only to a few per cent dissociated, the dissociation is nearly complete in the case of some other aryl derivatives. Schmidlin[3] has shown that the process of dissociation is not instantaneous but requires a short though appreciable time, and hence he was able to show that it is the colored substance which reacts rapidly with oxygen or iodine, thus exhibiting the characteristics of a free radical. Indeed it might be possible under favorable circumstances to obtain the degree of dissociation in a new way by rapid titration of the colored substance against atmospheric oxygen.

Gomberg has hesitated to adopt the conclusion that the colored triarylmethyls retain the benzoid form, on the ground that there is no analogy to support the assumption that a colored substance could be formed by the mere dissociation of a colorless substance such as the substituted ethane. It is true there is no analogy in organic chemistry except among these very compounds of trivalent carbon, and the corresponding compounds of bivalent and quadrivalent nitrogen which have been investigated with great perspicuity by Wieland and his collaborators. If, however, we examine the whole field of chemistry, we see that triphenylmethyl belongs to a class of substances which are almost invariably colored and which are typified by NO_2 which, like

triphenylmethyl, associates at low temperature or high concentration to form the colorless double molecule. They are the substances which possess what I have called, in a recent paper,[4] *odd molecules*.

I will review briefly the significance of this term. If we assume that every neutral atom possesses in its outer shell a number of electrons corresponding to the ordinal number of the element's group in the periodic system, for example, H, 1; C, 4; N, 5; O, 6; Cl, 7, then in almost all compounds there is an even number of such electrons. Those few substances which possess an odd or unpaired electron are said to have odd molecules. Thus sodium in the state of vapor has 1, monatomic iodine has 7, NO_2 has 17, ClO_2 has 19, $(C_6H_5)_3C$ has 91, $(C_6H_5)_2N$ has 63, and $(C_6H_5)_2NO$ has 69. Since an unpaired electron is always held in the molecule by weak constraints, it is usually capable of oscillating with so low a characteristic frequency as to absorb visible light. This absorption, moreover, involving only a single electron, might be expected to be of the simplest possible character.

In fact it has been shown by Wieland[5] that several substances of this type, with odd molecules, have very characteristic absorption spectra possessing ordinarily a single absorption band. Thus the spectrum not only of $(C_6H_5)_2NO$ but also of the triarylmethyls is like that of NO_2 and by no means resembles that of such quinoid substances as triphenylmethyl ion. There seems therefore every reason to believe that triphenylmethyl is colored not because it assumes the quinoid form but because it possesses an odd electron which, as in every other known substance of this class except NO, has a sufficiently low natural frequency to absorb visible light.

But whether or not this point be admitted, the fact that equilibrium is rapidly established between the ethanes and their corresponding methyls shows conclusively the non-existence of the first type of steric hindrance. Instead of a retardation due to the large groups we find a reaction velocity which, among organic compounds, is exceptionally high.

Therefore in the discussion of this type of reaction the term, steric hindrance, tacitly came to be employed in the second sense, implying a crowding out of large groups by other large groups, and this view seemed to be favored by the discovery by Schlenk that the degree of dissociation of the hexarylethanes ordinarily increases with increasing complexity of the substituted aryl groups.

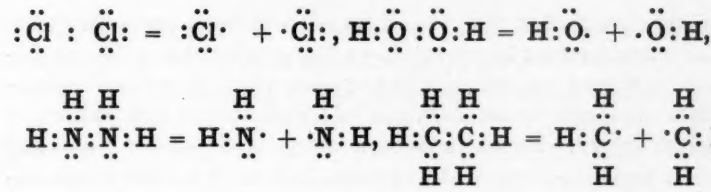
In order to obtain a comprehensive view let us consider four substances which in the light of the periodic system must in certain re-

spects be regarded as analogous, namely, Cl—Cl, HO—OH, H_2N—NH_2, H_3C—CH_3. The chlorine molecule acquiring rotational energy due to temperature has a certain tendency, through centrifugal force, to break at the bond of union into monatomic molecules. The molecule of bromine with its heavier atoms has, especially in view of modern quantum theory, a higher moment of momentum and is therefore dissociated to a higher degree, while iodine with its still heavier atoms is to a large degree dissociated at easily attainable temperatures. No one has suggested that this dissociation of iodine vapor is due to steric hindrance. The volume occupied by an atom is at best a most indefinite conception, but the atomic volume commonly attributed to iodine is not greater than that attributed to bromine or chlorine. It is doubtless the mass of the iodine atom which is chiefly responsible for its greater dissociation.

Since diatomic iodine dissociates to give nul-valent iodine we may expect to find a properly substituted hydrogen peroxide dissociate to give a compound of univalent oxygen, as the substituted hydrazines and ethanes have been found to give compounds of bivalent nitrogen and trivalent carbon. Both in hydrazine and in ethane it is the substitution of heavy groups which causes appreciable dissociation. Thus pentaphenylethane does not dissociate sufficiently to show the properties of a free radical below 180°, where it absorbs oxygen readily.[6] Hexaphenylethane is at room temperature dissociated to the extent of several per cent. The successive substitution of phenyl by biphenyl[7] increases the dissociation regularly. Now it is possible, but not obvious, that biphenyl occupies more space immediately about the methyl carbon than phenyl does. It certainly seems better to assume that by increasing the mass of the group and thus increasing the centrifugal force at the central bond, it produces a greater dissociation.

Another interesting illustration of the effect of the mass of the substituent upon dissociation is afforded by the interesting substance obtained by Wieland in which one oxygen of NO_2 is replaced by two phenyl groups. While NO_2 is largely associated even at ordinary temperatures $(C_6H_5)_2NO$ remains monomolecular even at the lowest temperature obtainable with solid CO_2 and ether.

The relation between nul-valent chlorine, univalent oxygen, bivalent nitrogen and trivalent carbon is more readily visualized if we express the equations of dissociation in the symbols of my previous paper:



The symbols in heavy type represent the atomic kernels, while the dots represent the electrons of the outer shells. It is the odd electrons that gives the free radicals color and high reactivity. It will be understood that the particular substances used for illustration are dissociated only to an extremely small degree; only upon substitution of heavier radicals will the dissociation be appreciable at ordinary temperatures.

In emphasizing the effect of mass and thus of centrifugal force in breaking a chemical bond we must not forget, however, that this is only one of the two main factors that determine the stability of a molecule. The other factor is the strength of the constraints which constitute the bond itself. (Electrochemical influences which are so frequently important do not concern us here since we are considering a bond symmetrically placed between two identical radicals.) I have pointed out, in the paper already cited, that the bond between two carbon atoms is weakened when either atom has a double bond or is attached directly to an atom with a double bond. Thus the great change produced by the substitution of phenyl for hydrogen or alkyl is due to both increasing mass and a weakened bond. If the phenyl groups in hexaphenylethane are replaced by the somewhat heavier benzyl groups the dissociation will nevertheless be diminished, since the benzyl will not aid in weakening the central bond. On the other hand there are radicals which cause a still greater weakening of the central bond than the phenyl group. Thus Gomberg has shown that the linking of two of the phenyl groups of triphenylmethyl by an atom of oxygen in the ortho positions greatly increases the percentage of free radical.

The odd molecules produced by the thermal dissociation of the substances here considered may combine not only with their like but with other free radicals to produce mixed types. Thus the reaction $(Ar)_2N-N(Ar)_2+(Ar)_3C-C(Ar)_3=2(Ar)_3C-N(Ar)_2$ is analogous to the reaction $(Ar)_3C-C(Ar)_3+I_2=2(Ar)_3C-I$. Wieland[8] has found a very interesting reversible reaction $(C_6H_5)_3C-C(C_6H_5)_3+(C_6H_5)_2N-N(C_6H_5)_2=2(C_6H_5)_3C-N(C_6H_5)_2$.

By some reaction of this type, if proper protection against intramolecular rearrangement be provided, we may predict that a di-aryl substituted hydrogen peroxide will be prepared, which in turn will dissociate into mono-aryl oxide, ArO, the odd molecule, or free radical, of univalent oxygen. Such a peroxide would probably be less dissociated than the similarly substituted hydrazine, just as the latter is less dissociated than the corresponding ethane.

[1] Gomberg, *J. Amer. Chem. Soc.*, **38**, 770 (1916).
[2] Piccard, *Liebig's Ann. Chem.*, **381**, 347 (1911).
[3] Schmidlin, *Ber. D. Chem. Ges.*, **41**, 2471 (1908).
[4] Lewis, *J. Amer. Chem. Soc.*, **38**, 770 (1916).
[5] Wieland and Offenbecher, *Ber. D. Chem. Ges.*, **47**, 2111 (1914); Meyer and Wieland, *Ibid.*, **44**, 2557 (1911).
[6] Chichibabin, *Ibid.*, **40**, 367 (1907).
[7] Schlenk, Weickel and Herzenstein, *Liebig's Ann. Chem.*, **372**, 1 (1910).
[8] Wieland, *Ibid.*, **381**, 200 (1911).

NEWTON'S METHOD IN GENERAL ANALYSIS

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The present paper is essentially an extension of the methods and results given by Dean H. B. Fine, On Newton's Method of Approximation,[1] and the results there obtained need not be explained here.

An illustration of some general notions.—As might be expected, Newton's Method is of very wide application and may be used, for example in the following three cases to find a real 'root' of the real functionelle $F[x(s)]$ where F has the property that in a certain domain, and for every $x(s)$ and $x(s)+h(s)$ in this domain, there exist functionelles F_1 and F_2 for which

$$F[x(s)+h(s)] \equiv F[x(s)]+\int_0^1 F_1[x(s),r]h(r)dr + \int_0^1\int_0^1 \tfrac{1}{2} F_2[\xi(s),r_1,r_2]h(r_1)h(r_2)\,dr_1\,dr_2, \qquad (A)$$

(1) where $\xi(s)$ is such that $\max_s |\xi(s)-x(s)| \leqq \max_s |h(s)|$ and $\max_s |x(s)+h(s)-\xi(s)| \leqq \max_s |h(s)|$, if by '$\max_s$' is meant the maximum as s varies, and by a 'root' of the above equation is meant a function $x(s)$, such that $\max_s |F[x(s)]| = 0$; or (2) where $\xi(s)$ is such that $\sqrt{\int_0^1[\xi(r)-x(r)]^2dr} \leqq \sqrt{\int_0^1 h^2(r)\,dr}$ and $\sqrt{\int_0^1[x(r)+h(r)-\xi(r)]^2dr} \leqq \sqrt{\int_0^1 h^2(r)\,dr}$, and by a 'root' is meant a function $x(s)$, such that $\sqrt{\int_0^1 F[x(r)]^2dr}=0$; or (3), where $\xi(s)$ is such that $\int_0^1 |\xi(r)-x(r)|\,dr \leqq$

$\int_0^1 | h(r) | dr$, and $\int_0^1 | x(r) + h(r) - \xi(r) | dr \leqq \int_0^1 | h(r) | dr$ and by a 'root' is meant a function $x(s)$ such that $\int_0^1 | F[x(r)] dr = 0$.

The above equation (A) we can write symbolically in the form

$$F(x+h) = F(x) + F'(x)h + \tfrac{1}{2} F''(\xi)h^2. \qquad (A')$$

We must regard x, h, and ξ as functions whose independent variables range over the same interval, viz., from zero to one. Any linear transformation of x must be accompanied by the same transformation on h and ξ. We shall speak of x, h, and ξ as covariant and of equal weight, viz., *one*, on the first of the two ranges that we shall consider. On the other hand the symbol h^2 or $h(r_1)\ h(r_2)$ is covariant with h but of weight *two*. Now h and F are not covariant, but *divariant*. We shall say that F is defined on the second range. Clearly F, F' and $\frac{1}{2} F''$ are covariant and of weight one on this second range. Similarly F' and h are *contravariant*, for only if F' be subjected to the transformation contragredient to that on h, will the term $F'h$ be left invariant. Similarly $\frac{1}{2} F''$ must be subjected to the square of the contragredient transformation. The whole situation may be succinctly expressed by introducing the notion of *signature*, which denotes the range and weight and whether covariant or contravariant. We shall say that x, h, and ξ are of signature (1, 0) being defined on the first but not on the second range, and of weight one on the first, h^2 is of signature (2,0) being of weight two. F is of signature (0, 1), F' of signature $(-1, 1)$ being contravariant with functions of weight one on the first range, and covariant with functions of weight one on the second, $\frac{1}{2} F''$ is of signature $(-2, 1)$. A constant we may speak of as of signature (0, 0).

The three expressions (1) $\max_s | z(s) |$, (2) $\sqrt{\int_0^1 z^2(r) dr}$, (3) $\int_0^1 | z(r) | dr$ we may subsume under the notation $\| z \|$ for the ranges (1, 0) and (0, 1). If the integration be in the sense of Lebesgue, it is true that if $z(s) = 0$ identically in s, then $\| z \| = 0$ in each of the cases, but in the second and third cases it does not follow from $\| z \| = 0$ that $z(s) = 0$ identically in s.

We may speak of x, h, ξ, F, F', $\frac{1}{2} F''$ as vectors, this being an extension of the familiar notion of a real vector in three dimensions. The symbolic expression (A') brings in symbolic products of apparently different types. But if the signature be kept in mind, no ambiguity results, for in each case, the product of two vectors has for its signature, the matrical sum of the signatures of the factors. For example in $\frac{1}{2} F''(\xi)h^2$, we have $(-2, 1) + (1, 0) + (1, 0) = (0, 1)$ as desired. The norm $\| z \|$ of the vector z may also be readily defined for $h^2\ F'$ and $\frac{1}{2} F''$, so

as to satisfy certain useful inequalities. We shall define in the three cases respectively; (1) $\| h^2 \| \equiv \max_{s_1 s_2} | h(s_1) h(s_2) |$, $\| F'[x(s), r] \| \equiv \max_s \int_0^1 | F[x(s), r] | dr$, $\| \frac{1}{2} F''[x(s), r_1, r_2] \| \equiv \max_s \int_0^1 \int_0^1 | \frac{1}{2} F''[x(s), r_1, r_2] | dr_1 dr_2$; (2) $\| h^2 \| \equiv \int_0^1 \int_0^1 h^2(r_1) h^2(r_2) dr_1 dr_2$, $\| F'[x(s), r] \| \equiv \sqrt{\int_0^1 \int_0^1 F'[x(s), r]^2 ds dr}$, $\| \frac{1}{2} F''[x(s), r_1, r_2] \| \equiv \sqrt{\int_0^1 \int_0^1 \int_0^1 \{\frac{1}{2} F''[x(s), r_1, r_2]\}^2 ds dr_1 dr_2}$; (3) $\| h^2 \| \equiv \int_0^1 \int_0^1 | h(r_1) h(r_2) | dr_1 dr_2$, $\| F'[x(s), r] \| \equiv \int_0^1 \{\max_r | F[x(s), r] | \} ds$, $| \frac{1}{2} F''[x(s), r_1, r_2] \| \equiv \int_0^1 \{\max_{r_1 r_2} | \frac{1}{2} F''[x(s), r_1, r_2] | \} ds$. With these definitions $\| z_1 + z_2 \| \leqq \| z_1 \| + \| z_2 \|$ and $\| z_1 z_2 \| \leqq \| z_1 \| \| z_2 \|$, where $z_1 z_2$ means the symbolic product. Furthermore we may define $\| z \|$ for z of range (0, 0) as identical with $| z |$.

The case of Newton's method for one variable and n variables has been discussed by Dean Fine in the paper referred to. These cases and the case of integration in which the ranges are continuous may be treated by the methods discussed in the present paper. But the conditions here used are of an abstract sort and may be used in much more extensive cases as will be clear to those familiar with the recent work of E. H. Moore, M. Fréchet, F. Riesz, V. Volterra, etc. The scalars, or vectors of signature (0, 0), which in all of the classical instances are ordinary real numbers, may be taken as Hensel p-adic numbers or elements in any *perjekte bewertete Körper* of Kürschák,[2] but more generally do not need to constitute a field as division is not essential. To avoid repetition the further discussion of this case will not be treated separately but may be regarded as included in the following sections.

Preliminary concepts.—Starting with an arbitrarily chosen range, which we shall refer to by the signature (1, 0), we shall suppose that we may construct ranges of the signatures (0, 0), (0, 1), (1, 1), (−1, 1), (−2, 1), (2, 0), respectively, where the range of signature (0, 0) contains but one element. An explicit definition of signature will not be required.

By the term *vector* or *function on a range*, will be meant a correspondence from the elements of a range to a set of *scalars* where each element determines one and only one scalar. A vector of signature (0, 0) is by definition a scalar, and conversely. The sum and the difference of two scalars will be required to exist uniquely, addition being associative. The sum and the difference of two vectors will be the usual vector or matrix sum and difference, respectively, and will be required to exist uniquely in the cases considered. The product of two vectors will be required to exist uniquely in the cases considered, and to be (1) associative, (2) completely distributive with respect to addition—so that addition is proved to be commutative, (3) continuous in each factor, continuity being defined as below, and (4) such that the signature of

the range of the product is the matrix sum of the signatures of the ranges of the factors.

The notation $\| z \|$ will be used for the *norm* of z. We shall require only that (1) $\| z \|, = \| -z \|$, is a uniquely defined real non-negative number such that $z \equiv 0$ implies $\| z \| = 0$, but not necessarily conversely; (2) $\| z_1 + z_2 \| \leqq \| z_1 \| + \| z_2 \|, \| z_1 z_2 \| \leqq \| z_1 \| \| z_2 \|$, and in particular, if $\| z_1 \| = 0$, $\| z_1 + z_2 \| = \| z_2 \|$, the sum and the product being defined as above; (3) the signature of z being given and a positive number ϵ, being given, there exists a z, such that $0 < \| z \| < \epsilon$; and (4) if $z_1, z_2, \ldots, z_n, \ldots$ be a denumerable sequence of vectors on the same range, and such that $\| z_1 \| + \| z_2 \| + \ldots + \| z_n \| + \ldots$ converges to a finite limit, then there is at least one z on the same range such that given any positive number ϵ, there exists a number m such that $n > m$ implies that $\| z - \Sigma_1^n z_i \| < \epsilon$ and $\lim_{n=\infty} \| \Sigma_1^n z_i \| = \| (z) \|$. Such a z will be called a *limit* of $z_1 + z_2 + \ldots + z_n + \ldots$, and we notice that for any two such limits z and z', $\| z - z' \| = 0$. We shall define two vectors z and z' for which $\| z - z' \| = 0$ as equivalent. It is by virtue of this last-named property that the vectors of a given range form in some sense a closed set.

A vector b with the signature $(-1, 1)$ will be said to be *non-singular*, if and only if there exists a unique vector b^{-1}, with the signature $(1, -1)$ such that the equation $a = bx$ where a is of signature $(0, 1)$, and x is required to be of signature $(1, 0)$, always has one and only one solution given by $x = b^{-1}a$.

We shall extend the usual definition of continuity to the case where $g(x)$ and x are of any signature as follows:—The function $g(x)$ is *continuous* in x at x' if for every assigned positive constant ϵ, there exists a positive constant δ, such that $\| x - x' \| < \delta$ implies that $\| g(x) - g(x') \| < \epsilon$.

Description of Newton's method.—In describing Newton's Method, we presuppose that we are given initially a function $f(x)$, where x is of signature $(1, 0)$ and $f(x)$ of signature $(0, 1)$, and such that we may expand $f(x+h)$ as follows:—

$$f(x+h) = f(x) + f'(x)h + \tfrac{1}{2} f''(\xi)h^2, \qquad (1)$$

where h and ξ are of signature $(1, 0)$, h^2 of signature $(2, 0)$, f' of signature $(-1, 1)$, f'' of signature $(-2, 1)$, the expansion being valid in a known domain. The ξ is supposed to be dependent on the x and h, but such that simultaneously $\| \xi - x \| \leqq \| h \|$ and $\| (x+h) - \xi \| \leqq \| h \|$. The functions f, f', and f'' are all supposed to be continuous in the domain considered. Equation (1) may also be written, for convenience, in the form $f(x+h) = a + bh + ch^2$.

Newton's Method consists in the following steps. Choose any x_0 in the domain and then select h_0 as a solution of $a_0+b_0h_0=0$. Put $x_1=x_0+h_0$, and repeat. Thus $a_i+b_ih_i=0$, and $x_{i+1}=x_i+h_i$, $i=0, 1, \ldots$, where in general a_i, b_i, c_i mean $a(x_i)$, $b(x_i)$, $c(x_i)$ respectively. If $\lim_{i=\infty} x_i$ exists uniquely, $(=x')$, and is in the domain, then x' is a root of $f(x)=0$.

In order that Newton's Method may be applied, we note that the equations $a_i+b_ih_i=0$ must be solved uniquely for h_i, so that $b(x)$ must be non-singular in the domain. We shall write $\| a_i\|=\alpha_i$, $\| b_i^{-1} \|=1/\beta_i$, $\| c_i \| =\gamma_i$. Taking the norm of both members of equation (1), and recalling that $a_i+b_i h_i=0$, we have $\| f(x_i+h_i) \|=\| c(\xi_i)h_i^2 \| \leqq \gamma_i \| h_i \|^2$. From $h_i=-b_i^{-1}a_i$, we have

$$\| h_i \| \leqq (1/\beta_i)\alpha_i, \tag{2}$$

Thus we may write

$$\alpha_{i+1} \leqq \gamma_i(1/\beta_i)^2\alpha_i^2 \text{ or } (\alpha_i\gamma_i/\beta_i^2)\alpha_i.$$

If the sequence of approximations x_i is to yield a root x' as a limit, it is necessary that the sequence of values of $\| f \|$, viz., $\alpha_{i+1}=\| f(x_{i+1}) \|=\| f(x_i+h_i) \|$ approach zero as a limit, and hence necessary although not sufficient that the limit of $(\alpha_i\gamma_i/\beta_i^2)$ shall not exceed unity. A refinement of these considerations suggests the theorems of the following section.

Justification of Newton's Method.—Theorem 1. *Let x_0 be given and let D be a positive number such that $f(x)$ is expansible in the form* (1) *for every x and $x+h$ (if either be denoted by u) in the domain $\| u-x_0 \| < D$. Let $f'(x)$ be non-singular in the domain, and B be a positive number such that $\| f^{-1}(x) \| < 1/B$ in the domain, and C a positive number such that $\| \frac{1}{2}f''(x) \| < C$ in the domain. Then Newton's Method yields a root x' in the domain, whenever $(CD/B) \geqq \varphi[C \| f(x_0) \| /B^2]$ where $\varphi(\lambda) \equiv \lambda+\lambda^2+\lambda^4+\lambda^8+\ldots+\lambda^{2^i}+\ldots$.*

An idea of the behavior of $\varphi(\lambda)$ may be had by noting that $\varphi(\lambda)$ has the unit circle in the complex plane for natural boundary, so that $\varphi(\lambda)$ is not defined for real positive λ's except when λ is not greater than one. Obviously $\varphi(\lambda)$ increases with positive λ's. Some of the numerical values of $\varphi(\lambda)$ are given by the following table.

λ	$\varphi(\lambda)$	λ	$\varphi(\lambda)$
0.	0.	0.566126	1.000000
0.1	0.110100	0.6	1.106678
0.2	0.241603	0.7	1.491062
0.3	0.398165	0.8	2.046305
0.356497	0.500000	0.9	3.017540
0.4	0.586255	1.	∞
0.5	0.816421	$\varphi[1/(k+1)] < 1/k, k > 0.$	

The proof of the above theorem is immediate. We shall use the previous notation. From (3), $\alpha_{i+1} \leqq (C/B^2)\alpha_i^2$, and from (2), $\| h_i \| \leqq (1/B)\alpha_i$. Hence $\| \Sigma_0^\infty h_i \| \leqq \Sigma_0^\infty \| h_i \| \leqq (1/B)[\alpha_0 + (C/B^2)\alpha_0^2 + (C/B^2)^3 \alpha_0^4 + \ldots + (C/B^2)^{2i-1}\alpha^{2^i} + \ldots] \leqq (B/C)\varphi[(C/B^2)\alpha_0]$. Thus if $\| \Sigma_0^\infty h_i \| = \| (x_0 + \Sigma_0^\infty h_i) - x_0 \| < D$, we have by hypothesis $x' = x_0 + \Sigma_0^\infty h_i$ as a vector in the domain, for which also $\lim_{i=\infty} \alpha_i = 0$.

Theorem 2. *If x' is a root of $f(x)$, and $\| f'(x')^{-1} \|$ exists and is equal to $1/\beta'$ and if $\| \frac{1}{2} f''(x) \| \leqq \beta'/D'$ in the region defined by $\| x - x' \| \leqq D'$ and if $f(x)$ is expansible in the form* (1) *in this region, then there is no other nonequivalent root of $f(x)$ in this region.*

Suppose if possible x'' is another nonequivalent root in the region. Then $f(x'') = f(x') + f'(x')(x'' - x') + \frac{1}{2} f''(\xi')(x'' - x')^2$ and since x' and x'' are roots of $f(x)$, the equation $f'(x')(x'' - x') = f(x'') - f(x') - \frac{1}{2} f''(\xi')(x'' - x')^2$ reduces to $\| x'' - x' \| = \| f'(x')^{-1} \| \cdot \| [-\frac{1}{2} f''(\xi')](x'' - x')^2 \|$ or $\| x'' - x' \| \leqq (1/\beta')(\beta'/D') \| x'' - x' \|^2$, so that since $\| x'' - x' \| \neq 0$, $\| x'' - x' \| \geqq D'$, contrary to hypothesis.

The following theorem is a corollary of Theorems 1 and 2 where $D' = 2D$. The proof is trivial and will be omitted.

Theorem 3. *Let x_0 be given and $f(x)$ be expansible in the form* (1) *in the domain $\| \bar{x} - x \| < B/(2C)$, these being defined as in Theorem 1. If $\| f(x_0) \| \leqq B^2/(3C)$, then Newton's Method yields a root x' in the domain and any root in the domain is equivalent to x'.*

Conclusion.—It may be noted that in these theorems no explicit use is made of h_0, x_1 and similar terms, derivable but not initially given. This feature and the statement of the general Theorems 1, and 2, as against Theorem 3, distinguish the form of these results from those of Dean H. B. Fine, already referred to. The steps in the proofs are in essential taken from the article by Dean Fine, where however the proofs hold only for a finite range, and are here extended to a general range, with a consequent notational simplification. The method here used of obtaining a general result by a mere reinterpretation of the case of one variable, offers several features of novelty and is suggested as, perhaps, of even more interest than the results obtained by its particular application to the present problem.

The present theory applies to nonlinear functionelles and integral equations with quadratic terms. A complete expansion in integral power series is not presupposed. In addition to interpretations of $\| z \|$ as $\sqrt{\Sigma z_{(n)}^2}$ and its generalizations, $\| z \|$ may be interpreted as $\max_n | z_{(n)} |$ or as $\Sigma | z_{(n)} |$ or in various other ways for the range (1, 0), with obvious extensions to the other cases. We may even with Riesz

(Equations Linéaires) introduce an arbitrary parameter p and write $\| z \| \equiv \sqrt[p]{\Sigma} | z_{(n)}^p |$ as an instance.

[1] H. B. Fine, these *Proceedings*, **2**, 546 (1916).
[2] J. Kürschak, *J. Math., Berlin*, **142**, 211–253 (1913).

THE COBALTAMMINES

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The metallic elements whose properties of aggregation are such that they have low atomic volumes, or high 'cohesion,' form a series of complex ammonia compounds whose stability seems to increase with the cohesion, or decrease with the atomic volume of the metallic aggregate. These complex ammonia compounds, or ammines are of peculiar interest because, like the hydrates, their structure has not yet been explained in a satisfactory way from the standpoint of ordinary valence theories. Werner, however, has developed a special theory of valence which seems to fit very well the chemical behavior of these particular compounds, whether or not it is in agreement with the general behavior of other chemical substances.

Now perhaps the most important point to be established with respect to a series of salts such as these ammines, is the type of each salt with reference to its ionization in solution. When we turn to the work of Werner and of other investigators in this field, it is found hat no work has been done which determines directly the type for these salts, although it might be considered that their molecular conductance as determined by Werner, together with their chemical action, makes it seem probable that they belong to the types according to which he has classified them.

The freezing-point method should give the most easy and certain method for the determination of the type of such salts as these, but it is just here that not only the work of other investigators, but even that of Werner[1] himself, does not agree with his theory. Since in this laboratory there is a double combination potentiometer system specially designed for us by Dr. W. P. White, to give with a fifty-couple copper-constantan thermocouple a reading to one twenty-thousandth of a degree, it seemed advisable to make for the first time a series of accurate freezing-point measurements upon the special series of cobaltammines which was most used by Werner in his work. The analyses were made by a Haber-Zeiss water interferometer, loaned to us by the Geophysical

Laboratory through the kindness of Drs. John Johnston and L. H. Adams. The only troublesome feature of the analyses was that caused by the color of these salts; and the difficulties encountered were such that it seems advisable in future work upon these salts to determine the concentration of the solutions by the conductivity method, since that method would render unnecessary the frequent gravimetric analyses which had to be resorted to, in order to make certain that the proper interferometric bands were being read.

In order to give a comparison of the results with those obtained formerly, the following table is inserted, which gives a few of our values of the equivalent freezing-point-lowerings ($\Delta t/N$) at rounded concentrations, upon a number of these salts, including the interesting isomeric salts dinitrotetrammine cobalt chloride (croceo) and dinitrotetrammine cobalt nitrate (flavo), which are shown by the freezing-point results to be of the di-ionic type. The values obtained by Werner and Herty and by Peterson are given within parentheses. The table also contains the corresponding values of the van't Hoff coefficient or mol-number i, and those of the percentage ionization (including those derived from the conductivity-ratio).

While the results of Werner and Herty were very severely criticised by Peterson,[2] it will be seen that they are of the right order of magnitude, while Peterson's own results are about 100% too large, a divergence difficult to explain. The table shows that, while for the croceo salt the values of Werner and Herty are only about 8% too low, for the hexammine they obtained values which were so high (see figure) as to indicate that they belong to other types of salts than is the case; but on the whole the deviations of their results are explained by the fact that they used a Beckmann thermometer, and by the fact that most of the cobaltammines are not very soluble, so that the measurements have to be made in very dilute solutions, which makes the percentage accuracy much less than it would be at such concentrations as are commonly used.

The salts investigated are given in the following list, together with the number of ions which we have found that each salt produces.

	Ions
Hexammine (luteo) cobalt chloride	4
Nitropentammine (xantho) cobalt chloride	3
Chloropentammine (purpureo) cobalt chloride	3
Dinitrotetrammine (flavo) cobalt chloride	2
Dinitrotetrammine (croceo) cobalt chloride	2
Trinitrotriammine cobalt	0
Potassium tetranitrodiammine cobaltate	2
Ammonium tetranitrodiammine cobaltate	2
Sodium cobaltic nitrate	4

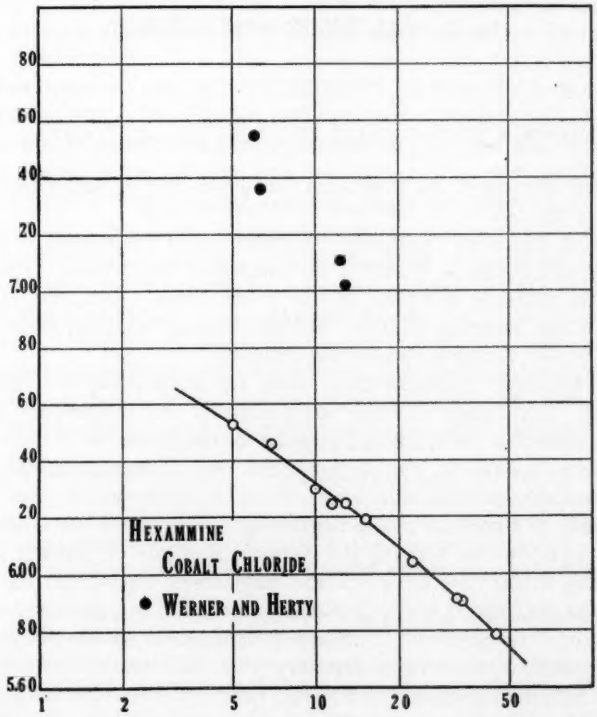
TABLE I

Concentration in milli-equivalents	Equiv. fr. pt. lowering $\Delta t/N$	Mol-number i for the cobaltammine	Mol-number i for potassium iodate	Percentage Fr.-Pt. Lower	Ionization from Conductivity
		Flavo Cobalt Nitrate			
2	3.65	1.964	1.967	96.4	96.6
5	3.595	1.935	1.958	93.5	93.8
(5)	(7.00)*				
10	3.531	1.900	1.937	90.0	91.2
(10)	(6.60)*				
20	3.446	1.855	1.908	85.5	
(20)	(6.15)*				
		Croceo Cobalt Chloride			
2	3.66	1.97	1.967	97.0	95.4
(4.35)	(3.45)†				
(4.72)	(3.60)†				
5	3.622	1.949	1.958	94.9	93.2
10	3.590	1.932	1.937	93.2	90.7
20	3.556	1.914	1.908	91.4	
		Hexammine Cobalt Chloride			
5	6.53	3.51		83.7	
(6)†	(7.54)	(4.055)			
	(7.36)	(3.95)			
10	6.32	3.40		80.0	
(12)†	(7.11)				
	(7.02)				
20	6.09	3.22		74.0	
50	5.74	3.09		69.0	
		Chloro-pentammine Cobalt Chloride			
5	5.35	2.88		94.0	
10	5.18	2.785		89.0	
20	4.95	2.66		83.0	
		Nitro-pentammine Cobalt Chloride			
5	5.26	2.83		91.5	
10	5.13	2.76		88.0	
20	4.935	2.655		82.7	
		Potassium tetra-nitro-diammine			
2	3.675	1.975		97.5	
5	3.65	1.95		95.	
10	3.62	1.945		94.5	
20	3.57	1.92		92.	
50	3.505	1.885		88.5	
		Ammonium tetra-nitro-diammine			
2	3.66	1.95		95.	
5	3.62	1.945		94.5	
10	3.565	1.92		92	
20	3.49	1.88		88.	

* Peterson. † Werner and Herty.

These results are in accord with Werner's theory in so far as the number of ions is concerned.

When the apparent ionization values for these salts obtained by the conductivity and freezing-point methods are compared, it is found that they are closely similar, except in the case of the tetraionic salt, when the result calculated from the freezing-point is much the higher. The deviation is in such a direction as could be explained by the theory of Harkins[4] that all salts of this and other higher types give a considerable



percentage of intermediate ions in solutions of about 0.1 normal concentration. It is of course realized that the apparent ionizations obtained by the two methods are in no cases directly comparable, since we do not know the variation in the activity of the different components.

While many of the cobaltammines are unstable and hydrolyze rapidly at higher temperatures, at zero degrees no trouble was experienced, except with dinitrotetrammine cobalt chloride when it was exposed to a bright light, and with sodium cobaltic nitrite.

The writers wish to express their indebtedness to the National Academy of Sciences for a grant of two hundred dollars from the Wolcott Gibbs Fund, which has been used to purchase the apparatus for this work. The complete paper will be published in the *Journal of the American Chemical Society*.

[1] Werner and Herty, *Zs. physik. Chem.*, **38**, 331 (1901).
[2] Petersen, *Zs. physik. Chem.*, **22**, 410 (1897); **39**, 249 (1902).
[3] Harkins, *J. Amer. Chem. Soc.*, **33**, 1807–73 (1911).

NATIONAL RESEARCH COUNCIL

REPORT OF THE FIRST MEETING OF THE COUNCIL

The first meeting of the Research Council was held in New York City on September 20, 1916.

Dr. M. I. Pupin, as Temporary Chairman, called the meeting to order at 3.10 p.m., and directed a roll-call of the members of the Council. There were present the following members: Messrs. Carty, Dunn, Goss, Hale, Herschel, Holmes, Keen, Manning, Marvin, Millikan, Noyes, Pickering, Pupin, Rand, Skinner, Squier, Stratton, Swasey and Vaughan.

The Temporary Chairman then called for nominations for Permanent Chairman. Dr. George E. Hale was nominated and unanimously elected. Dr. Hale then took the Chair and presided for the remainder of the meeting. Dr. Charles D. Walcott was elected First Vice-Chairman, and Mr. Gano Dunn, Second Vice-Chairman.

Dr. Hale, as Chairman of the Organizing Committee of the Council, announced an agreement between the National Academy of Sciences and the Engineering Foundation by which the Engineering Foundation has placed its funds at the disposal of the Council for a period of one year and has given the services of its Secretary, Dr. Cary T. Hutchinson, to the National Research Council, to serve as its Secretary. Dr. Hale announced that in accordance with this agreement the National Academy of Sciences has appointed Dr. Hutchinson Secretary of the National Research Council. Dr. Hutchinson was present and acted as Secretary to the meeting.

The Chairman then gave an extended account of the work done by the Organizing Committee during the summer months, dwelling particularly upon his trip to England and France, and upon the results that have been reached there by similar organizations of the men of science.

At the conclusion of the Chairman's remarks the organization of the Council was discussed; and the motion was made that an Executive Committee to consist of a chairman and nine members be appointed by the Chair, with the Chairman of the Council and President of the Academy as additional mem-

bers ex officiis, this Committee to have full authority in the interim between meetings of the Council to carry out the purposes described in the Preliminary Report of the Organizing Committee (published in the August number of these PROCEEDINGS), it being understood that, in carrying out the general plan of work of the Council as there outlined, the Executive Committee shall not be limited to a narrow interpretation of the objects, but shall have full power to undertake similar or related work, even though not specifically included in that report. This motion was carried unanimously.

The Chairman then requested the members of the Council to express their views on the proposed work of the Council, and in particular to make suggestions covering definite lines of work that might fall within the sphere of activity of the Council.

Dr. Keen reported that upon notification of his selection to the Council he had made a careful investigation of the attitude of the colleges and medical schools in the vicinity of Philadelphia and that all approved the objects of the Research Council and would give their best support to it; also that the American Philosophical Society would co-operate with the Research Council in every particular. Professor Pickering dwelt on the opportunity for co-operation in astronomical work. Dr. Pupin spoke at length on the great value of co-operation in industrial research, as evidenced by the work of the Research Laboratory of the General Electric Company; he emphasized the difficulties in securing men adequately trained. Professor Conklin cited the results accomplished by co-operative effort in zoological work at the Woods Hole Biological Station, which he stated has passed resolutions endorsing the work of the Research Council and promising co-operation, as follows:

WHEREAS, the National Academy of Sciences at the request of President Wilson has taken the initiative in bringing into co-operation existing governmental, educational, industrial and other research organizations and has brought about the establishment of a National Research Council which shall be representative of these various organizations, and whose object shall be the promotion of scientific research with especial reference to national welfare; and

WHEREAS, the Marine Biological Laboratory is a striking illustration of the value of co-operation in the promotion of scientific research; and

WHEREAS, we believe that human progress depends upon increasing knowledge of nature and that national welfare can most effectively be advanced by the co-operation of scientific investigators;

Now, Therefore, be it resolved, that the Trustees of the Marine Biological Laboratory approve of the establishment of a National Research Council and agree to co-operate in all practicable ways in its work of co-ordinating and promoting scientific research.

Dr. Noyes called attention to the need of urging universities and colleges to interest more men in research work and to train them for it more effectively. Dr. Carty dwelt on the essential identity between pure and applied research, pointing out that they do not differ in kind but merely in the objects to be accomplished; that industrial research has as its objective commercial or industrial development, and that scientific research has no such immediate pur-

pose. Colonel Squier spoke at some length on his experience in England during the past four or five months in communication with the War Department; he dwelt on the vital importance of pure scientific research and predicted that the United States will probably find it desirable to appoint as a cabinet officer a Secretary of Sciences in the not distant future. Dr. Stratton emphasized the growing need of more and better training of men for research work. Dr. Goss deprecated the distinction between pure and applied science, claiming that such distinction did not in reality exist and that all was science. Dr. Vaughan believed that much good could be done by the Council in stimulating the Congress of the United States to make greater appropriations to help pure science, and instanced the mean support given by the Government in many cases. Mr. Manning dwelt briefly upon the work of the Bureau of Mines and outlined the assistance given to the Bureau of Mines by the great chemical and smelting companies; he suggested similar assistance in the development of pure scientific research.

Dr. Millikan then presented a preliminary report for the Committee on the Newlands' Bill, which provides for the appropriation by the Government of $15,000 annually to each of the states, to be applied to research in engineering and applied science. After discussion the report was referred back to the Committee for further consideration with instructions that it be then referred to the Executive Committee of the Research Council.

A recess was then taken to enable the members of the Council to attend a dinner given in their honor at the University Club by Dr. George E. Hale.

The Council was called to order at 9.30 p.m. by the Chairman. The same members were present as at the afternoon meeting. Mr. Melville Stone, manager of the Associated Press, was also present as a guest of the Council.

At the invitation of the Chairman, the members discussed special features of the work that the Council might undertake.

Dr. Keen emphasized the necessity for making available the advances in surgery during the war. Dr. Vaughan emphasized the importance of this. Dr. Pupin spoke generally on the value of the proposed work of the Council. Dr. Holmes spoke of the possibilities of development in anthropological work and promised to present his views in writing later. Prof. Marvin believed it to be desirable to conduct a campaign of education to bring to congressmen a realization of the importance of scientific research.

Dr. Noyes made a general report on the work done by the Nitrate Supply Committee, of which he is the Chairman. He thought also that much good could be accomplished by encouraging the publication of a journal of popular science which should emphasize the relations of science, and especially of scientific research, to the public welfare, and that this might be done in co-operation with the American Association for the Advancement of Science.

Mr. Rand dwelt upon the essential need of co-operation with the great industrial research organizations, instanced the assistance that the Research Laboratories of the U. S. Steel Corporation had rendered to the Institute of

Mining Engineers, and expressed the belief that the co-operation of the U. S. Steel Corporation with the Research Council could readily be secured. Mr. Skinner outlined the work of the Westinghouse Research Laboratory and suggested specifically investigations on fuel for internal engines, on the prevention of corrosion, and on vocational diseases. Mr. Herschel pledged the support of the American Society of Civil Engineers, Dr. Goss dwelt on the necessity of co-operation in institutions of the Middle West, and suggested a committee on relations of the universities to the National Research Council.

Dr. Vaughan called attention to the need of proper means of publicity, and Mr. Melville Stone, the guest of the Council, made a forceful address on the relations of the Associated Press to men of science and pledged the firm support of his organization to the objects of the Research Council.

Mr. Dunn outlined in considerable detail the relations of the Engineering Foundation to the National Research Council and praised the generosity of Mr. Swasey in giving his liberal support to the Foundation. Mr. Swasey in reply minimized his own share in the development of the Foundation. He suggested that a committee on optical and commercial glass would find a large field for useful work.

The Chairman announced the appointment of the following six members of the Executive Committee: Messrs. J. J. Carty, E. G. Conklin, Gano Dunn, A. A. Noyes, M. I. Pupin and V. C. Vaughan. He stated that the other four members would be appointed after further consideration.

It was voted that the Council should meet at the call of the Executive Committee.

A vote of thanks to the Chairman for his invaluable services was unanimously adopted.

After further general discussion the meeting adjourned at 11.30 p.m.

CARY T. HUTCHINSON, *Secretary.*

REPORTS OF MEETINGS OF THE EXECUTIVE COMMITTEE

The first meeting of the Executive Committee was held in New York on September 21, 1916. There were present Messrs. J. J. Carty, E. G. Conklin, Gano Dunn, G. E. Hale, A. A. Noyes, Michael Pupin and V. C. Vaughan, and C. T. Hutchinson the Secretary of the Council.

Dr. J. J. Carty was elected Chairman; and Dr. C. T. Hutchinson, Secretary of the Committee.

It was voted that the terms of the present members of the Research Council and of the Executive Committee be deemed to expire on January 1, 1918.

The following resolution was adopted, expressing the general policy to be followed by the Council in the promotion of research.

Resolved, that the efforts of the Research Council shall be uniformly directed to the encouragement of individual initiative in research work, and that co-operation and organization,

as understood by the Research Council, shall not be deemed to involve restrictions or limitations of any kind to be placed upon research workers.

The following resolution was adopted, inviting the American Association for the Advancement of Science to co-operate with the Research Council.

Resolved, that the American Association for the Advancement of Science be informed that the National Research Council has been organized by the National Academy of Sciences at the request of the President of the United States for the purpose of bringing into co-operation existing governmental, educational, industrial, and other research organizations, with the object of encouraging the investigation of natural phenomena, the increased use of scientific research in the development of American industries, the employment of scientific methods in strengthening the national defense, and such other applications of science as will promote the national security and welfare; and that the Association, which has itself established the Committee of One Hundred on Research, be invited to co-operate with the Research Council in the promotion of research, and that to this end it be asked to appoint a committee of three to meet with a similar committee of the Research Council to consider how such co-operation can be made most effective.

As members of this Committee on behalf of the Research Council, Dr. Welch, president of the Academy, and Messrs. Conklin and Noyes were appointed.

The following committees were also appointed:

A committee to arrange for an office for the Research Council in the Engineering Societies Building, consisting of Messrs. Pupin and Dunn.

A Committee on Rules and Procedure, consisting of Messrs. J. J. Carty (Chairman), E. G. Conklin and A. A. Noyes.

A Committee on Publication, of which Mr. Gano Dunn was made Chairman and given power to name his associates.

A Committee on Research in Educational Institutions, consisting of G. E. Hale, Chairman, J. S. Ames, R. H. Chittenden, J. M. Coulter, G. N. Lewis, G. H. Parker, Harold Pender, C. R. Van Hise and F. J. E. Woodbridge; this committee to consider general plans for the promotion of research in educational institutions, and to have power to arrange for local committees in each institution.

A Committee on the Promotion of Industrial Research, Dr. J. J. Carty, Chairman, with functions in its field somewhat similar to those of the Committee on Research in Educational Institutions.

A Committee on a National Census of Research, Dr. Stratton, Chairman, to prepare a national census of equipment for research, of the men engaged in it, and of the lines of investigation pursued in co-operating Government bureaus, educational institutions, research foundations, and industrial research laboratories.

The second meeting of the Executive Committee was held in New York on September 29, 1916. Messrs. J. J. Carty, E. G. Conklin, Gano Dunn, G. E. Hale, A. A. Noyes, Michael Pupin, V. C. Vaughan, W. H. Welch and the Secretary were present.

Mr. Dunn reported that the United Engineering Society had granted for a period of one year from October 1, 1916, free of assessment, rooms number 901 and 902, for the use of the Engineering Foundation, to serve as New York office for the National Research Council, these rooms being those about to be vacated by the Naval Consulting Board.

After considerable discussion of the financial affairs of the Council it was voted that a Committee on Finance, to consist of three members, should be appointed by the Chairman to consider the question of obtaining additional funds for the Research Council and the method of handling such funds as it has or as it may acquire.

It was voted to recommend to the President of the Academy that Dr. Marston T. Bogert, of Columbia University, Dr. Russell H. Chittenden, of Yale University, and Dr. Raymond Pearl, of the Maine Agricultural Experiment Station, be invited to become members of the Council.

It was voted that joint committees on research in various branches of science be formed in cooperation with the corresponding national scientific societies.

Dr. Vaughan was also asked to report on the need of research in the preparation of therapeutic agents.

Dr. S. W. Stratton of the Bureau of Standards, and Dr. Raymond Pearl of the Maine Agricultural Station were appointed members of the Executive Committee by the Chairman of the Research Council.

CARY T. HUTCHINSON, *Secretary.*

ORGANIZATION OF THE RESEARCH COUNCIL

The National Research Council was formally organized at a meeting held in New York City on September 20, 1916. It was established by the National Academy of Sciences at the request of the President of the United States. The members of this Council have been appointed by the President of the Academy, after consultation with the presidents of leading national scientific societies. The representatives of the Government were appointed by the President of the United States. The Council is to be gradually enlarged by the addition of new members who are to serve as chairmen of important committees or who are otherwise to engage in some special capacity in the work of the Council.

The organization of the Council is at present as follows:

OFFICERS AND EXECUTIVE COMMITTEE

Chairman, GEORGE E. HALE.
Vice-Chairmen, CHARLES D. WALCOTT and GANO DUNN.
Secretary, CARY T. HUTCHINSON.
Executive Committee, JOHN J. CARTY (Chairman), WILLIAM H. WELCH (ex officio), GEORGE E. HALE (ex officio), EDWIN G. CONKLIN, GANO DUNN, ARTHUR A. NOYES, RAYMOND PEARL, MICHAEL I. PUPIN, S. W. STRATTON, V. C. VAUGHAN (others to be appointed).

MEMBERS

Dr. L. H. Baekeland, Yonkers, N. Y.
Dr. Marston T. Bogert, Professor of Organic Chemistry, Columbia University.
Dr. John A. Brashear, Allegheny, Pa.
Dr. John J. Carty, Chief Engineer, American Telephone and Telegraph Co.
Dr. Russell H. Chittenden, Director, Sheffield Scientific School, Yale University.
Dr. Edwin G. Conklin, Professor of Zoology, Princeton University.
Dr. John M. Coulter, Professor of Botany, University of Chicago.
Major-General William Crozier, Chief of Ordnance, U. S. A.
Mr. Gano Dunn, President, The J. G. White Engineering Corporation.
Dr. Simon Flexner, Director, Rockefeller Medical Institute.
Brigadier-General William Crawford Gorgas, Surgeon-General, U. S. A.
Dr. W. F. M. Goss, Dean of Engineering, University of Illinois.
Dr. George E. Hale, Director, Mt. Wilson Solar Observatory.
Mr. Clemens Herschel, President, American Society of Civil Engineers.
Dr. William H. Holmes, Curator, United States National Museum.
Dr. W. W. Keen, President, American Philosophical Society.
Mr. Van H. Manning, Director, Bureau of Mines.
Prof. Charles F. Marvin, Chief, United States Weather Bureau
Prof. A. A. Michelson, Director, Ryerson Physical Laboratory, University of Chicago.
Dr. Robert A. Millikan, Professor of Physics, University of Chicago.
Dr. Arthur A. Noyes, Director, Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.
Dr. Raymond Pearl, Director, Maine Agricultural Experiment Station.
Prof. E. C. Pickering, Director, Harvard College Observatory.
Dr. Michael I. Pupin, Professor of Electro-Mechanics, Columbia University.
Mr. Charles F. Rand, President, United Engineering Society.
Dr. Theodore W. Richards, Director, Walcott Gibbs Memorial Laboratory, Harvard University.
Mr. C. E. Skinner, Director, Research Laboratory, Westinghouse Electric and Manufacturing Co.
Lieutenant-Colonel George O. Squier, Chief of Aviation, U. S. A.
Dr. S. W. Stratton, Director, Bureau of Standards.
Mr. Ambrose Swasey, Cleveland, Ohio.
Chief Constructor David W. Taylor, U. S. Navy.
Dr. Elihu Thomson, Swampscott, Mass.
Dr. C. R. Van Hise, President, American Association for the Advancement of Science.
Dr. Victor Clarence Vaughan, Director, Medical Research Laboratory.
Dr. Charles D. Walcott, Secretary, Smithsonian Institution.
Dr. William H. Welch, President, National Academy of Sciences.
Dr. W. R. Whitney, Director, Research Laboratory, General Electric Co.